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Special lectures

Laws of Thermodynamics

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acknowledgement and warning

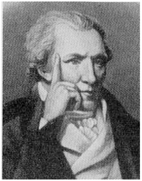
acknowledgement:

- Thanks to Prof T Amaranath and V D Sharma for the invitation
- warning :
- I am going to talk about
  - the essential contents of the laws of thermodynamics, tracing
    - their origin, and
    - their history
  - The Zeroth law, the First law the Second law .....and may be the Third law, if time permits
  - I leave it to your imagination to connect my talks to the theme of the School which is MECHANICS.

- Each law provides an experimental basis for a thermodynamic property
  - Zeroth law $\Longrightarrow$ Temperature, T
  - First law $\Longrightarrow$ Internal Energy, U
  - Second law $\Longrightarrow$ Entropy, S
- The earliest was the Second law discovered in the year 1824 by Sadi Carnot (1796-1832)


Sadi Carnot


Helmholtz


Rumford


Mayer


Joule

- then came the First law - a few decades later, when Helmholtz consolidated and abstracted the experimental findings of Rumford, Mayer and Joule into a law.
- the Zeroth law arrived only in the twentieth century, and I think Max Planck was responsible for it

VOCALUBARY

- System: The small part of the universe under consideration: *e.g.*
    - a piece of iron
    - a glass of water
    - an engine
- The rest of the universe (in which we stand and make observations and measurements on the system) is called the surroundings
- a glass of water is the system and the room in which the glass is placed is called the surrounding.
- the system and the surroundings together is called the universe

- the surrounding is often idealized as a bath :
- we are familiar with the heath bath or thermostat;
- we can think of work bath.
- the key idea is that the bath influences the system;
- the bath itself does not get influenced by the system
- *e.g.* keep a cup of hot coffee in this room
- coffee is the system
- the room is the bath.
- the coffee cools until it attains the temperature of the room
- the room does not get heated up because of the presence of hot coffee
- strictly, we should say, when the coffee cools, the room temperature increases by an extremely small amount which for all practical purposes can be ignored;
- hence we call the room as a heat bath

- a system has a boundary
- if matter can be exchanged between the system and the surrounding through its boundary we call it OPEN
- the boundary is permeable and dia-thermic
- a bucket of water is an open system
- A system with a boundary that does not permit exchange of matter is called CLOSED
- the boundary is dia-thermic but not permeable
- a sealed bottle is a closed system

- a system with a boundary that is impervious to whatever is happening in the surroundsings is called an
  ISOLATED system
- its boundary or wall is adiabatic - meaning *impassable*
- an isolated system remains unchanged regardless of what happens in the surroundings
- any change that happens in the system is called adiabatic change or adiabatic process
- adiabatic processes are important in a fundamental way to the very formulation of thermodynamics

- a closed vacuum flask holding hot cup of coffee is an isolated system
- the properties of a system can be classified as extensive and intensive
- extensive property: it is one which depends on the quantity of matter present in the system. *e.g.*

  • mass • volume • energy • entropy • free energy
- intensive property : one that is independent of the quantity of matter present in the system *e.g.* • temperature • pressure • chemical potential

- often we construct an intensive variable by dividing one extensive variable by another extensive variable *e.g.*
    - density : mass/volume ;
    - specific heat : heat capacity / mass
    - specific volume : volume / number of molecules;
- Mathematically,

$$f(\lambda x, \lambda y) = \lambda f(x, y)$$

f is extensive; it is a function of x and y, which are extensive variables

- f is first order homogeneous in x and y

examples of Extensive or additive thermodynamic variables:

$$\begin{aligned} \text{energy} &: U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N) \\ \text{Free energy} &: F(T, \lambda V, \lambda N) = \lambda F(T, V, N) \\ \text{Enthalpy} &: H(\lambda S, P, \lambda N) = \lambda H(S, P, N) \\ \text{Gibbs free energy} &: G(T, P, \lambda N) = \lambda G(T, P, N) \end{aligned}$$

- Mechanical Equilibrium:
- Consider two horizontal cylinders each fitted with a piston containing gas.
  - the left cylinder is sealed in the left face
  - the right cylinder is sealed in the right face
  - the two pistons are connected by a rigid rod in the middle;
  - the connecting rod is clamped
- let us release the clamp and observe what happens;

- Scenario - 1
- both the pistons move to the right;
- from this we surmise that the gas in the left cylinder is at higher pressure than the gas in the right
- hence the gas in the left cylinder expands and pushes the piston to its right
- its pressure decreases
- as a result the piston in the right cylinder moves to the right compressing the gas in it
- its pressure increases
- eventually the two pressures are equalized and the pistons stop moving

- Scenario - 2
- both the pistons move to the left.
- gas in the right cylinder is under higher pressure;
- it expands and pushes the piston to its left
- the piston in the left cylinder moves to its left
- the gas in left cylinder is compressed
- the pistons stop moving once pressures are equalized

- Scenario -3
- the pistons do not move at all when we release the clamp
- nothing happens
- when nothing happens, physicists are delighted
- they get interested only when nothing happens
- they conclude the two systems are in mechanical equilibrium with each other
- equality of pressure implies mechanical equilibrium
- Let us call these two cylinders A and B
- now we de-link A and B; then we link B to another cylinder C

- let us say we find that B is in mechanical equilibrium with C
- then we know what would happen when we link A with C
- we do not need to to carry out the experiment;
- we can anticipate ... we can predict that A and C would be in mechanical equilibrium with each other
- mechanical equilibrium is transitive binary relation
- *pressure is a universal indicator of mechanical equilibrium*
- let us move from mechanics to thermodynamics and to the realm of zeroth law

- consider system A with a rigid wall made of a metal as its boundary
- System B also has rigid metal wall as its boundary
- System A and B are put in contact with each other
- we observe HEAT flows from either A to B or B to A.
    - What is Heat ?
    - we shall come to it shortly;
    - we need to come to the first law to find what heat is
    - When nothing happens *i.e.* when no change occurs in the properties of A and B, when no heat flows, either from A to B or from B to A, then we say A and B are in thermal equilibrium with each other

- We now de-link A and B
- and establish thermal contact between B and a third system C;
- if nothing happens *i.e.* no heat flow from B to C or from C to B, we say that the systems B and C are in thermal equilibrium with each other
- we can now anticipate what would happen if we bring A and C into thermal contact with eath other;
- nothing would happen; they would be in thermal equilibrium with each other
- we do not need to carry out the experiment

- Thermal equilibrium is a transitive binary relation
- this simple observation constitutes the essential content of the zeroth law of thermodynamics
- zeroth implies that there should exist a property that enables us to anticipate when two systems are found in thermal equilibrium with each other
- there should exist a universal indicator of thermal equilibrium
- such a universal property is called temperature
- all systems, (irrespective of their individual nature, mechanical, electrical, magnetic, or otherwise) which are in thermal equilibrium with each other are at the same temperature

- Thus the zeroth law gives an experimental basis for the existance of a thermdynamic property called temperature
- However the zeroth law does not give any clue about how to measure temperature
- before we leave the zeroth law and go to first law, we need to clarify the term HEAT used in ther description
- Heat: A sensation of warmth or coldness we feel when we touch a body.
- By touching we can tell a hot body from a cold body, most of the time
- but touching can be deceptive

- Consider the following experiment
- on your left you have a glass of cold water
- on your right you have a glass of warm water
- in the middle you have a glass of water at room temperature
- dip your right and left fingers in the middle glass
- you will feel the same sensation in both the fingers
- both the fingers tell you that the water in the middle glass is neither cold nor warm;
- you are happy : you can judge the thermal state water in the middle glass by touching

- now dip your right finger in the right glass, and the left finger in the left glass
- the right finger feels warm; the left finger feels cold
- you are happy : by touching you are able to deistinguish between hot and cold
- but then ... watch out

- now dip both fingers in the middle glass
- what do you feel ?
- your right finger feels cold; it tells you the water in middle glass is cold
- but your left finger feels hot; it tells you the water in the middle glass is warm
- which finger would you believe - the right or left ?
- however you know both the fingers are lying
- you know the water in the middle glass is neither cold nor hot !
- now tell me, can you believe touching as a means of determining the thermal state of a body ?

- Touching is of little help when it comes to a quantitative scientific measure of the thermal state of a body;
- we need precise terminologies and tools.
- this leads to the notion of empirical temperature
- the volume of a body increases upon heating : *thermal expansion.*
- Thermal expansion coefficient is given by

$$\gamma = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \ K^{-1}$$

- this gives us a way of measuring the thermal state of a body

- We can tell whether a body gets hotter or colder, by a purely mechanical observation of the change of its volume.
- Thus born the empirical Temperature
- take a substance with good thermal conductivity and make a thermometer
- that was what Daniel Fahrenheit (1686 - 1736) and Anders Celcius (1701 - 1744) did
- they used mercury

- We are all familiar with the temperature scales devised by Fahrenheit and Celcius
- Fahrenheit took body temperature as 100 $^\circ$; in his scale water freezes at 32 $^\circ$ F nad boils at 212 $^\circ$ F.
- Celcius took 0 $^\circ$ C as the temperature at which water freezes and 100 $^\circ$ F as that at which water boils.
- much later Lord Kelvin (1824 - 1927) came up with an absoulte scale temperature based on the Second law of thermodynamics *i.e.* Carnot's engine,
- I am not going to talk about these scales of temperatures
- different kinds of thermometers have been built, based on change in other properties

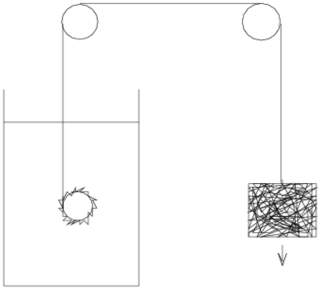
- I am not going to talk about these thermometers
- instead, let us get on with our enquiries about the nature of heat
- An important finding from experiments of measuring temperatures with thermometers is the following :
- Heat flows spontaneously from a body at a higher temperature to a body at a lower temperature when these two bodies are brought into thermal contact with each other.
- this means that heat is an entity
- it is a massless, colourless, tasteless fluid;
- call it calorique in French or caloric in English

- *a fluid flows from a higher to a lower elevation.*
- *Caloric flows from hot to cold i.e.* from higher to lower temperature
- caloric flows down a temperature gradient
- But then we know now this caloric picture is wrong
- but we are stuck with terms like heat absorption; heat flow; heat transport; *etc*
- It was Benjamin Thompson Rumford (1753 - 1814), Julius Robert von Mayer (1814 - 1878), and James Prescot Joule (1818 - 1889) who showed us that caroric theory of heat was wrong
- They laid the foundation for the formulation of the first law of thermodynamics

- Rumford noticed in 1798 that a canon became hot while boring.
  - the heat generated is sufficient to melt the canon if it could be returned to the metal
  - this implies that the heat released from the metal is more than what it contained originally
    - something not possible under Caloric theory.
  - Rumford concluded correctly that it is the mechanical work that got converted to heat.
  - he also estimated approximately the mechanical equivalent of heat.
  - physicists of his day ignored his findings.

- Mayer estimated mechanical equivalent of heat based on his experiments with horses stirring paper pulp in a cauldron.
    - nobody took notice of the above work.
- Heat from friction was attributed to the Caloric fluid being squeezed out of the body!

- Then came Joule with his paddle wheel



- measured change in temperature produced by friction of a rotating paddle-wheel immersed in water;

- the paddle wheel is attached to a weight
- the falling weight rotates the wheel;
- the ‘ falling distance ’ and the weight measures the work done.
- Joule carried out a series of measurements and found that one calorie equals 4.15 N m, which agrees with the current accepted value, see box below, within 1%, a remarkable feat indeed!
- $1 Nm = 1 Joule$

$$\boxed{1 \text{ Cal. } = 4.184 \text{ J}}$$

- The experiments of Rumford, Mayer and Joule established unambiguously that

heat is equivalent to work

- this identification led to the formulation of the first law of thermodynamics
- Of the four laws of thermodynamics the one that is easiest to grasp is the first law because
- it is an extension of the law of *conservation of energy*
- What is energy and why should it be conserved
- to answer this question let us start with something we are familiar with

- let us start with the notion of work as we find it in dynamics
- the term work arises in the context of motion against an opposing force
- we do work when we raise a weight against the opposing force of gravity
  - like pulling up a bucket of water from a deep well with a rope passing over a simple pulley
- we do work when we climb up the stairs
  - raising our weight against gravity

- how much work we do, depends on
  - the mass of the object being raised
    - the mass of water in the bucket that is being pulled
    - how heavy you are when you climb the stairs
  - the strength of the gravitational pull
    - on the moon you will do less work when you pull a bucket of water from a well
    - on the moon you will do less work when you climb up the stairs
    - but then on the moon you will be paid less !!
  - the height through which the object is raised against gravity
    - how deep the well is
    - how many stairs you need to climb

- you do work when cycling against the wind
    - the stronger the wind the more is the work you do;
    - the farther you cycle, the more is the work you do;
    - the heavier you are, the more would be the work you do
- you do work when you stretch a spring or when you compress a spring
- the work depends on
    - the strength of the spring and
    - the distance through which it is stretched or compressed

- When you raise 50 kg through a height of 2 meters, you do work of 980 kg m^2 s^{-2} or 980 joules.
- thus every system has a capacity to do work
- *i.e.* it can raise a weight through a distance against gravity
    - a compressed spring can do work
    - an extended spring can do work
    - an electric battery can do work
    - *etc*
- we need a special term to denote the capacity of a system to do work
- this capacity to do work we term as internal energy

- a spring stretched more can deliver larger quantum of work than a spring stretched less
- we can say the same thing as follows :
- a spring stretched more has higher energy than a spring stretched less
- let us extend this concept of energy from dynamics to thermodynamics
- consider a system enclosed in adiabatic walls - *i.e.* thermally non-conducting walls
- the system is thermally insulated
- a thermos flask containing water is an example

- churn the contents of the flask with paddle, driven by a falling weight
- we know how much of work is done by the falling weight; let it be W
- we can measure the rise in the temperature with a thermometer; let it be ΔT
- now remove the insulation and allow the system to return to its original state
- put back the adiabatic wall; insert a heater; pass an electric current for a duration which does the same (electrical) work W
- find the rise in temperature;
- it will be ΔT

- we can do the same work on the insulated system by several other ways
- the rise in the temperature shall be same in all these experiments
- from these observations we conclude :
  when the work done is the same in a thermally insulated system the change in temperature is the same
- it does't matter how have you delivered the work
- let us describe this in a more formal language

- Consider a thermodynamic process that takes a system from one equilibrium state A to another equilibrium state B
- the work done, in general, will depend on the actual path taken during the process
- work is path dependent
- work is a process variable, not a state variable
- there is an exception to this general rule

- consider the process $A \to B$ to be adiabatic.
- then the work done depends only on the initial and final states
- work done is independent of the path, when carried out adiabatically *i.e.* when carried out on a thermally insulated system
- this recognition that work done is independent of the path, in an adiabatic process, gives us a powerful means of defining a thermodynamic state variable called internal energy U

- Take a reference equilibrium state say A
- Define a state variable called internal energy U at A and set it to a value say $U(A) = 0$
- Then, we can map all other points in the phase plane in terms of internal energy, by considering adiabatic processes that connect A to each of these points
- consider a state B; go to B from A adiabatically and find the work done, W_{adia}
- Define $U(B) - U(A) = W_{adia}$

- if you can not go from A to B adiabatically then you will definitely be able to go from B to A adiabatically
- thus $\Delta U = U(B) - U(A) = W_{adia}$ - the adiabatic work done in going from A to B
- now consider going from A to B by a non adiabatic process
- let the work done be W
- calculate the difference $W_{adia} - W$, between adiabatic work and non-adiabatic work
- this difference is called HEAT, Q
- $Q = W_{adia} - W = \Delta U - W$

- The statement

$$Q = \Delta U - W$$

  is called the first law of thermodynamics
- Let us rearrange the terms and write

$$\Delta U = Q + W$$

- we can transact energy between a system and its surroundings
  - by heat or
  - by work

  which are two modes of transfer of energy

- we need to make a few observations before we leave the first law and take on the more-difficult-to-grasp second law of thermodynamics
- first we must recognize that heat is a process variable; not a state variable
- heat is not an entity;
- heat is not a content of a body
- it makes no sense to ask how much heat is contained in a body
- like it makes no sense to ask of how much work is contained in a body
- heat is not even a form of energy

- heat is a mode of transfer of energy by virtue of difference in temperature
- heat is energy in transit, when the transit is caused by temperature gradient
- work is energy in transit, when the transit is caused by pressure difference
- it is like this :
- we know rumour spreads;
- this doesn't make rumour a fluid !

- we know energy spreads
    - when it spreads by virtue of temperature difference, we call it heat;
    - when it spreads by virtue of pressure difference we call it work
- this doesn't make heat a fluid;
- Notice we never call work a fluid
- notice we never make statements like the following
    - work flows from body A to body B
    - work is added to a system
    - work is transferred from A to B
    - work is transported
    - *etc.*

- the first law has established the equivalence of heat and work
- but even today we continue to make statements like
  - *heat flows from body A to body B*
  - *heat is added to a system*
  - *heat is transfered from A ton B*
  - *heat is transported*
  - *etc.*
- these phrases and sentences are indelibly embedded in our language; in our discourse

- these are consequences of our caloric past
- we shall continue to use these phrases purely as a matter of convenience
- but then we shall do it with full awareness that these words and sentences can not be taken to be literally true;
- we shall do so with an understanding these words and sentences are short hand notations
- now is time to move on to the more intriguing law of thermodynamics - the second law
- in doing so we will pretend we are in the caloric world
- this will help us obtain a historical perspective

- experiments showed that heat can generate pressure
  - heat water in a closed vessel and produce steam;
  - the steam is at very high pressure
  - think of a pressure cooker
- pressure difference can make objects move
- man asked : can we make heat move objects
- he started working on conversion of heat in to work
- heat engines became prevalent
- they started dotting the country side in the early years of the nineteenth century

Leonard Sadi Carnot (1796 - 1832)
(discoverer of the Second law)

Reflexions on the motive power of fire and on machines to develop that power (1824)

started working on the theory of extracting mechanical work from sources of heat.

- for Sadi Carnot, the very idea of a heat engine was amazing
- a heat engine converts heat into work;
- it produces movement from heat.
- In nature it is the movement that generates heat;
- we call it friction;
- there is no phenomenon like un-friction;

- heat generated in friction does not reassemble to give rise to motion.
- Carnot found heat engine to be analogous to a water mill
- water falling from height h_1 to height h_2 sets the mill into motion
- caloric heat falling from temperature T_1 to T_2 produces movement
- if q_1 calories of heat were to fall from T_1 to zero, then we would get work $w = q_1$;
- the efficiency of the engine would be $\eta = w/q_1 = 1$.
- But then heat falls from T_1 to $T_2 \neq 0$. In fact $T_1 > T_2 > 0$

- Hence only a fraction given by

$$\frac{T_1 - T_2}{T_1 - 0}$$

  of q would be converted into work
- the efficiency would be

$$\eta = \frac{w}{q_1} = 1 - \frac{T_2}{T_1} \; < \; 1 \; .$$

- Carnot rightly identified that mere production of heat is not sufficient to produce work;
- it is necessary there should be cold;
- without it heat it would be useless.

- heat engine requires flow of heat;
- heat flows only when there is a temperature difference;
- you need a hot boiler and a cold radiator or cooling tower
- Carnot concluded that
  the amount of energy you get out as useful work from a machine is always less than the heat you put in.
- a machine working in a cycle, can convert a given amount W of " mechanical energy ". completely into equivalent q of " heat energy ".
- the converse is not possible.

- a given amount q of " heat energy " can not be completely converted into equivalent amount W of mechanical energy (work).
- the road is one way; the only way is down (- the drain!)
- we have to pay a penalty whenever we want to convert heat into work.
- this is the essense of the Second Law of thermodynamics
- Scientists did not recognize the fundamental import of Carnot's discovery for more than two decades.
- It was Carnot's friend,

  Benoit Paul Emilie Clapeyron (1799 - 1864)

  who kept the knowledge alive.

- in the year 1834 Clapeyron gave a mathematical formulation to the work of Carnot;
- the familiar $P - V$ diagram of Carnot's engine is the work of Clapeyron
- it was this work that caught the attention of Kelvin and Clausius in the early fifties of the nineteenth century.
  - **Lord Kelvin** (1824 - 1907)

  rejected Carnot's reasoning; but *found Carnot's conclusion correct* and accepted it as fundamental axiom: **the Second law**.
- In Kelvin's words of 1852, the Second law goes as,
  - "It is impossible for a self-acting machine unaided by any external agency, to convey heat from one body to another at a higher temperature".

Rudolf Julius Emmanuel Clausius (1822 - 1888),

two year later worded the Second law as,

"Heat can not by itself pass from a colder body to a warmer body".

- How do we reconcile with the basic

$$\text{WORK} \Rightarrow \text{HEAT}$$

$$\text{WORK} \leftarrow \text{HEAT}$$

irreversibility?

- Before we comprehend irreversibility let us attend to the immediate and important task of
  " quantifying " reversibility.

- To this end Clausius in his 1865 paper on

  the kind of motion we call heat

  invented a new thermodynamic variable **Entropy**.
- Entropy: the transformational content of a body.
- derived from the Greek work $\tau\rho\pi\eta$ which means transformation.
- Clausius:

  > “I have intentionally formed the word **entropy** so as to be as similar as possible to the word *energy*; for, the two magnitudes to be denoted by these words are so nearly allied in their physical meanings that a certain similarity in designation appears to be desirable”

- Let $đ q$ be the heat absorbed by the system from a reservoir;
- $đ q$ is not a perfect differential;
- q is not a state function.

What do we mean by a perfect differential ?

What do we mean by a state function ?

- Consider a function $f(x, y)$; we have,

$$\begin{aligned} df &= \frac{\partial f}{\partial x}\ dx + \frac{\partial f}{\partial y}\ dy \\ df &= \Phi_1(x, y)\ dx + \Phi_2(x, y)\ dy \end{aligned}$$

- We have,

$$\frac{\partial \Phi_1}{\partial y} = \frac{\partial \Phi_2}{\partial x}$$

which is the same as

$$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)$$

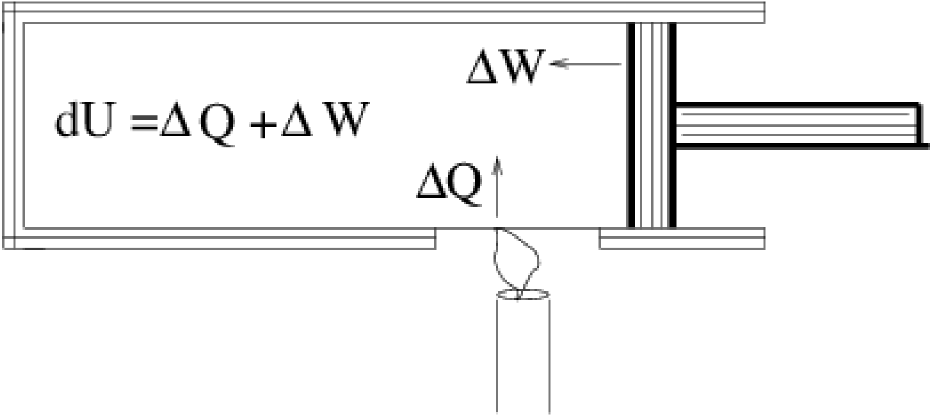
or

$$\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y}$$

the above obtains because,

- $f(x, y)$ is a (state) function of the (state) variables x and y; and
- df is a perfect differential.
- Let us investigate:
    - Is q a state function of the thermodynamic variables Temperature (T) and Pressure (P)?
    - Is Δq a perfect differential ?

Energy can be added to a system by work - push a piston and/or by heat, keep the system in fire



$$\Delta U = \Delta q + \Delta W;$$

- ΔU is a perfect differential;
- U is a state function;
- hence $dU = \Delta U$
- ΔW is not a perfect differential;
- the work done depends on the path
- W is not a state function;
- hence we say $đW = \Delta W$
- but

$$dV = -\frac{đW}{P}$$

is a perfect differential

- therefore we have,

$$\begin{aligned}
dU &= \Delta q - PdV \\
\Delta q &= dU + PdV \\
&= C_V dT + PdV : \Big[PV = Nk_B T; \text{(Ideal gas)} \\
&\qquad\qquad dV = Nk_B \left(\frac{1}{P} dT - \frac{T}{P^2} dP \right) \Big] \\
&= C_V dT + PNk_B \left(\frac{1}{P} dT - \frac{T}{P^2} dP \right) \\
&= (C_V + Nk_B) dT - \left(\frac{Nk_B T}{P} \right) dP
\end{aligned}$$

- Therefore we have,

$$\begin{aligned}\Phi_1(T,P) &= C_V + Nk_B \\ \Phi_2(T,P) &= -\frac{Nk_B T}{P}\end{aligned}$$

- It is easily verified that

$$\frac{\partial \Phi_1}{\partial P} \neq \frac{\partial \Phi_2}{\partial T}$$

  LHS is zero and the RHS is $-Nk_B/P$.

- q is not a state function; Δq is not a perfect differential; hence the notation $đq$.

- What should we do to construct a state function so that we can describe heat exchanges ?

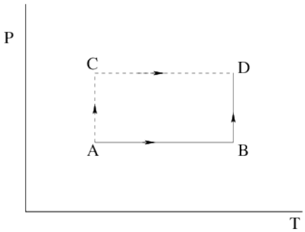
$$\text{Consider} \quad dS = \frac{đq}{T}.$$

We have,

$$\begin{aligned} \frac{đq}{T} &= \frac{dU}{T} + P\frac{dV}{T} \\ dS &= (C_V + Nk_B)\frac{dT}{T} - Nk_B\frac{dP}{P} \end{aligned}$$

- It is easily verified that,

$$\frac{\partial}{\partial P}\left(\frac{\partial S}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right) = 0$$



Heat exchanged is dependent on the path:

$$\begin{aligned} \text{đ}Q(\text{path}:A \to B \to D) &= C_P(T_D - T_A) - nR\,T_D \log(P_D/P_A) \\ \text{đ}Q(\text{path}:A \to C \to D) &= C_P(T_D - T_A) - nR\,T_A \log(P_D/p_A) \end{aligned}$$

Entropy change is independent of the path:

$$\begin{aligned} dS(\text{path}:A \to B \to D) &= C_P \log(T_D/T_A) - nR \log(P_D/P_A) \\ &= dS(\text{path}:A \to C \to D) \end{aligned}$$

- Therefore $S \equiv S(T, P)$ is a state function and dS is a perfect differential.
- Thus $đq$ is not a perfect differential; but once we divide it by T it becomes a perfect differential.
- Clausius named S as entropy.
- It is meaningless to ask : "How much of heat is there in a body ?" .
- However it is quite fine to ask: "How much entropy is there in a body ?"
- Notice however, Clausius defines only dS - the **change** in entropy; and not absolute entropy.
- We have to wait for more than half a century for Boltzmann to come and define absolute entropy.
- What does this imply? Why is this important ?

- For a meaningful interpretation of Clausius' definition of (change of) entropy we need to define
    - a thermodynamic process in which
        - a macroscopic system switches from one equilibrium state to another equilibrium state

          and
        - during the switching process the system remains in equilibrium.
- Clausius called such a process *quasi-static* and reversible.

- Consider the following switching experiment:
  - a classical macroscopic system is in thermal equilibrium with a heath bath at $T = 1/[k_B\beta]$.
  - λ is an a external degree of freedom of the system which can be controlled from outside:

    e.g.

    - the system is a gas contained in a cylinder

      and

    - the degree of freedom λ is its volume which can be controlled from outside by moving a piston.

- For convenience, we normalize λ in such a way that it switches from zero to unity during the experiment;
- without loss of generality we assume that switching takes place at a constant rate;
- Let t_s denote the switching time; the switching rate is therefore $1/t_s$. *i.e.*

$$\begin{aligned} \frac{d\lambda}{dt} &= \frac{1}{t_s}; \\ \lambda(t) &= \frac{t}{t_s}. \end{aligned}$$

- For purpose of defining entropy, Clausius considers an ideal scenario: *the switching is carried out infinitely slowly, i.e.* $t_s = \infty$.
- a process of slow stepping through equilibrium states;
  - at each step the state variables assume the relationship given by the equilibrium equation of state;
- the system is sort of dragged through a dense succession of equilibrium states.
- The process is described by a path in the space of thermodynamic variables and the path contains only equilibrium states.

- quasi-static process : an ordered succession of equilibrium microstates.
- real process : a temporal succession of equilibrium and nonequilibrium microstates;
- identification of $(-Pdv)$ as mechanical work and (TdS) as the heat transfer is valid only for quasistatic processes.
- quasistatic locus can be approximated to a real process only if entropy is monotonically non-decreasing along the quasistatic locus.
- the limiting case of a quasistatic process in which the increase in entropy becomes vanishingly small is called a reversible process: $S(\mathrm{initial}) = S(\mathrm{final})$; *the process can be traversed in either direction.*

- Thus the very definition of (Clausius') entropy demands that the system during the entire switching process should remain in equilibrium.
- The change in entropy of the reservoir is

$$dS = -\frac{đ q_R}{T}$$

- The change of entropy of the system is

$$dS = +\frac{đ q_R}{T}$$

quasi-static processes are not realized in practice. Note: $t_s = \infty$; they are called ideal processes.

- however, such idealizations have immense value: the very definition of Entropy (and Free energies) is based on such ideal thermodynamic processes.
- In any process let dS denote the total change in entropy; it includes the change in entropy of the system and of its surroundings; the Second law asserts that $dS \ge 0$, and the equality obtains in a quasi-static reversible process.
- If $dS = 0$ there is no dissipation; If $dS > 0$, we say there is dissipation.
- Intuitively, dissipation means that energy from systematic modes has been redistributed into random (heat) modes.

- Usually several processes tend to become dissipationless when they are sufficiently slowed down.
- However there are dissipative processes that remain forever dissipative irrespective of their (non-zero) speeds. *e.g.* friction; heat conduction.
- In the ideal scenario considered, the process is not only reversible but also isothermal; therefore we have

$$dS = -\frac{đq}{T} = \frac{W_R}{T} = -\frac{PdV}{T}$$

- In general the Second law demands that,

$$dS \geq \frac{đq}{T}$$

  and the equality obtains when the process is reversible
- For an isothermal and reversible process, we have,

$$\begin{aligned} dU &= TdS + W_R \ \text{(First Law)} \\ d(U - TS) &= W_R \ \text{(Isothermal process)} \\ dF &= W_R \end{aligned}$$

Herman von Helmholtz (1821 - 1894)

$$F(T, V, N) = U(S, V, N) - TS(U, V, N)$$

- $F \equiv F(T, V, N)$ is called Helmholtz free energy.
- $F(T, V, N)$ is useful in the study of closed systems.
- Notice again
  - in thermodynamics it is the change in free energy, denoted by dF which is defined through an a reversible isothermal process;
  - absolute free energy is not defined.
- If the process is not reversible *i.e.* $t_s < \infty$) we have $dF < W$ and the difference $W - dF$ is called dissipative work done on the system and is denoted by W_d

- In general we have,

$$dF \le W$$

  equality obtains when the process is reversible
- $dF \ \le \ W$ is an equivalent statement of the Second law.
- Statements of second law in the context of irreversible processes involve inequalities and not equalities $dS \ > \ 0$; $dS \ > \ \text{đ}q/T$; $dF \ < \ W$ *etc.*
- Can we describe irreversible processes in terms of equalities
- The answer is yes and they constitute the recent trends in thermodynamics
- I shall tell of one such equality toward the end

$dS \geq \frac{\text{đ}q}{T}$ is equivalent to $dF \leq W$

$$
\begin{aligned}
dS &\geq \frac{\text{đ}q}{T} \\
\text{From the First Law } dU &= \text{đ}q + W \\
\text{Therefore } \text{đ}q &= dU - W \\
dS \geq \frac{\text{đ}q}{T} \Rightarrow dS &\geq \frac{dU - W}{T} \\
TdS - dU &\geq -W \\
-(dU - TdS) &\geq -W \\
d(U - TS) &\leq W \\
dF &\leq W
\end{aligned}
$$

Work⇒Heat→Work irreversibility

- Let us examine how Clausius' assertion

$$\boxed{dS \geq 0}$$

(called the Second law)

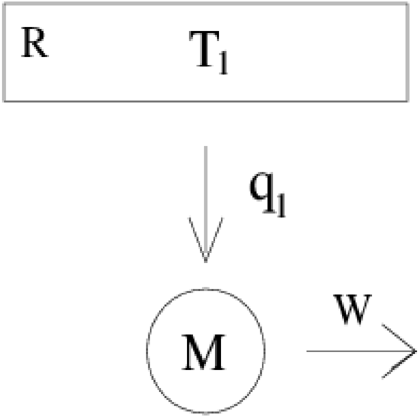
helps us understand the

$$\text{WORK} \Rightarrow \text{HEAT}$$

$$\text{WORK} \leftarrow \text{HEAT}$$

irreversibility.

Perfect Engine ($W = q_1$)



Perfect Engine and the Second Law

- A machine draws q_1 quantity of energy from a reservoir in the form of heat quasi-statically (reversibly) and isothermally at temperature T_1.
- it converts the whole of q_1 into work W and
- returns to its original thermodynamic state to start all over again.
- the above process is perfectly fine as far as the first law is concerned: energy is conserved.
- **Is it permitted under the Second law ?**

Second Law forbids Perfect Engine

$$\begin{aligned} \text{Total increase in entropy} &= dS \\ \text{Increase inentropy of the reservoir} &= dS_R \\ \text{Increase inentropy of the machine} &= dS_M \end{aligned}$$

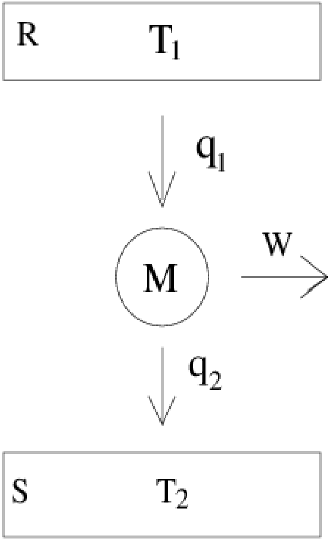
$$\begin{aligned} dS &= dS_R + dS_M \geq 0 \\ dS_R &= -\frac{q_1}{T_1};\ dS_M = 0; \\ -\frac{q_1}{T_1} &\geq 0 \end{aligned}$$

- If we demand $W = q_1$, we must have, as per the Second law,

$$-\frac{W}{T_1} \geq 0;\ \frac{W}{T_1} \leq 0;\ W \leq 0$$

- **the machine can not deliver positive work!**
- complete conversion of q_1 to equivalent W is impossible.
- does it mean that we can never extract work from heat?
- NO. it does not mean that.
- we can always construct an IDEAL engine.
- this is called Carnot's engine.

CARNOT'S IDEAL ENGINE



the Second law permits Carnot's Engine

- extract q_1 amount of energy from the reservoir (R) in the form of heat at temperature T_1.
- convert part of it into work.
- dump the remaining $q_2 = q_1 - W \ < q_1$ into a heat Sink (S) at a *lower* temperature T_2.
- it is the dumping that helps you meet the requirement of the Second law.

$$dS_R = -\frac{q_1}{T_1};\ dS_M = 0;\ dS_S = +\frac{q_2}{T_2}$$

$$dS = -\frac{q_1}{T_1} + \frac{q_2}{T_2} \geq 0$$

- Ideal engine implies that

$$\begin{aligned} dS &= 0; \text{ and hence } \frac{q_1}{T_1} = \frac{q_2}{T_2}; \\ W &= q_1 - q_2 \ \text{(energy is conserved)} \\ \eta &= \frac{W}{q_1} = 1 - \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1} \end{aligned}$$

- In general

  $$\eta \le 1 - \frac{T_2}{T_1}$$

  and the equality obtains for a quasi-static process.

- Thus even an ideal engine for which $dS = 0$, has an efficiency $\eta < 1$, for $T_2 \ne 0$. Thus the assertion $dS \ge 0$ explains Carnot's finding.

- Thus the Second law requirement that $dS \geq 0$ explains the irreversibility,

$$\text{WORK} \Rightarrow \text{HEAT}$$

$$\text{WORK} \leftarrow \text{HEAT}$$

- Thus Claussius, by introducing a new thermodynamic variable, called entropy, S, and demanding $dS \geq 0$ for any process, explained Carnot's finding

- Carnot's engine is an idealization; indeed it is a

  double idealization.

  - the efficiency is unity only when the temperature of the Sink is zero; *this not realistic*
  - the engine works in the quasi-static limit; the process is carried out infinitely slowly; the time required to complete a cycle is infinity; *this is not realistic either*
- any practical engine has an efficiency lower than Carnot's engine which itself has a perfect efficiency of unity only when the Sink temperature is at absolute zero.

From Thermodynamics to Statistical Mechanics

- a typical macroscopic object: a glass of water: it contains nearly 10^{25} water molecules.
- each molecule for complete specification requires three position and three momentum coordinates; in the spirit of coarse graining we ignore the structure of a molecules and the structure of its constituents.
- we need therefore $\sim 6 \times 10^{25}$ numbers to specify the macroscopic object.
- the system at a microscopic level is indeed hyperactive; the molecules are incessantly in motion;

- the system is switching from one microstate to another, all the time;
- each molecule moves as per the diktats of the Newtonian mechanics.
- the entire system of N molecules is specified by a point in a $6N$ dimensional phase space.
- the point traces out a trajectory in the phase space as per Newton's laws.
- consider an isolated system in equilibrium
- let us say that we are assured that the (isolated and equilibrium) system visits all the regions of the phase space accessible to it ' uniformly ' ;

- in other words the system spends equal duration of time in equal regions of the phase space.
- experimentally measured macroscopic property can be considered as a time average over the phase space trajectory traced by the system during a measurement.
- then, we can completely ignore the dynamics and calculate a macroscopic property as an average over a static Gibbs ensemble of microstates - with *all the microstates being equally probable.*
- this is called averaging over a microcanonical ensemble.

- notice that despite tremendous activity at a microscopic level, the macroscopic properties of the equilibrium system remain robust and unchanging.
  - water boils at 100 degree Celsius at standard pressure.
  - ice melts at zero degree Celsius.
  - pressure times volume remains the same for a given quantity of an ideal gas at constant temperature.
  - mercury expands upon heating.
  - when two bodies come into thermal contact, the hotter body cools and the colder warms up until both attain the same temperature.

- a few macroscopic descriptors like volume V, pressure P, entropy S, temperature T, density ρ *etc.* are adequate to describe the macroscopic state of the system.
- what is the reason for the observed robustness of a macroscopic behaviour ?
  - let us say you are determining a macroscopic property O, of a system by observing it over a duration of time say τ;
  - what you measure can be thought of as an average of the macroscopic property over the N microstates visited by the system during the experimental observation time τ. Let us denote it by $\overline{O}_N$; it is quite clear $\overline{O}_N$ is a random variable.

- if N is very large and if (we assume that) the microstates visited are all independent of each other, then $\overline{O}_N$ has a Gaussian distribution; this is a consequence of the Central Limit Theorem.
- more importantly, the variance of the Gaussian distribution is of the order of the inverse of N and hence is small for large N;
- since N is invariably large, we find a macroscopic property robust and unchanging with time.
- *e.g.* pressure is average momentum transferred to the wall (of the container) by the colliding molecules of the fluid. This is the simplest of micro-macro connections.
- in fact statistical mechanics establishes several such micro-macro connections.

The Central Limit Theorem

- $\{X_i\}$ are identically distributed independent random variables with mean μ and finite variance σ^2.
  Let $\rho(x)$ denote its probability density function.
- The characteristic function of X is

$$\begin{aligned}\Phi_X(k) &= \int_{-\infty}^{\infty} dx \exp[+ikx]\rho(x) \\ &= \exp\left[ik\mu - \frac{k^2}{2}\sigma^2 + \sum_{n=3}^{\infty} \frac{(ik)^n}{n!}\zeta_n\right]\end{aligned}$$

- In the above ζ_n is the n-th cumulant of X;

$$\zeta_1 = \mu \ ; \quad \zeta_2 = \sigma^2 .$$

The Central Limit Theorem...continued

$$Y = \frac{1}{N}(X_1 + X_2 + \cdots + X_N)$$

- The characteristic function of the random variable Y is:

$$\begin{aligned}
\Phi_Y(k) &= \left[\Phi_X\left(k \to \frac{k}{N}\right)\right]^N \\
&= \exp\left[ik\mu - \frac{k^2}{2}\frac{\sigma^2}{N} + \sum_{n=3}^{\infty}\frac{(ik)^n}{n!}\frac{\zeta_n}{N^{n-1}}\right] \\
&\underset{N\to\infty}{\sim} \exp\left[ik\mu - \frac{k^2}{2}\frac{\sigma^2}{N}\right]
\end{aligned}$$

- The above is a Gaussian whose Fourier inverse is also a Gaussian with mean μ and variance σ^2/N.

The Central Limit Theorem...continued

- For $N \to \infty$, we have strictly
$$\Phi_Y(k) = \exp[i\mu k]$$
whose Fourier inverse is
$$\delta(y - \mu);$$
- Y is not anymore random; it is deterministic;
- The macroscopic variable is robust indeed.
- For N adequately large, the fluctuations of Y is inversely proportional to $\sqrt{N}$ and hence is small.

MICRO - MACRO CONNECTION

Ludwig Boltzmann

(20 Feb. 1844 - 5 Oct. 1906)

$$\boxed{S = k_B \log(\hat{\Omega})}$$

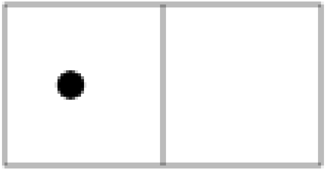
S is entropy

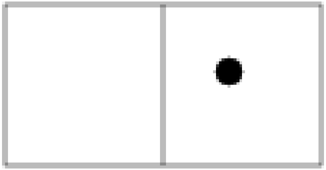
k_B is called the Boltzmann constant:
1.381×10^{-23} Joules per degree Kelvin or
8.671×0^{-5} electron-volt per degree Kelvin
$\hat{\Omega}$ is the number of microstates
accessible to the system

S for a toy model: one particle in a box of two portions

- Consider the following experiments:
  - take a particle and place it in a box; left or right portion.

Question	:	How many ways can you do this?
Answer	:	2; $\hat{\Omega} = 2$; $S = k_B \log 2$

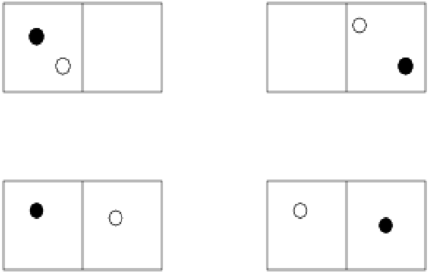




S for a toy model: two particles in a box of two portions

- take two particles (non interacting) and place them in the box independently.

Question	:	How many ways can you do this?
Answer	:	4; $\hat{\Omega} = 4$; $S = 2\ k_B \log 2$



S for a toy model: N particles in a box of two portions

- take N particles and place them in the box independently;

Question	How many ways can you do this?
Answer	$2^N;\ \hat{\Omega} = 2^N;\ S = N\ k_B \log 2$

- In the above experiments the box was divided into two equal parts. Consider an experiment of
  placing N particles independently in a box divided into 3 equal parts.

Question	How many ways can you do this?
Answer	$3^N;\ \hat{\Omega} = 3^N;\ S = N\ k_B \log 3$

S for a toy model: N particles in a abox of V portions

- Consider an experiment of placing N molecules independently in a box divided into V equal parts.

$$\begin{aligned} \text{Question} &: \text{How many ways can you do this?} \\ \text{Answer} &: V^N;\ \hat{\Omega} = V^N;\ S = N\ k_B \log V \end{aligned}$$

$$\begin{aligned} S &= k_B \log \hat{\Omega} = N k_B \log V \\ \frac{\partial S}{\partial V} &= \frac{N k_B}{V} = \frac{P}{T} \quad \text{(see box below)} \\ P\ V &= N\ k_B\ T \end{aligned}$$

- We have derived the ideal gas law!

S and dS

$$\begin{aligned}
S &\equiv S(U,V,N)\\
dS &= \left.\frac{\partial S}{\partial U}\right)_{V,N} dU + \left.\frac{\partial S}{\partial V}\right)_{U,N} dV + \left.\frac{\partial S}{\partial N}\right)_{U,V} dN\\
&= \left(\frac{1}{T}\right) \quad dU + \left(\frac{P}{T}\right) \quad dV + \left(-\frac{\mu}{T}\right) dN
\end{aligned}$$

- What more? Consider a thermodynamic process in which only the volume changes and all other thermodynamic variables remain the same. We have,

dS for the toy model

$$\begin{aligned} S(V) &= k_B N \log V \\ dS &= \frac{\partial S}{\partial V}\ dV = \frac{k_B N}{V}\ dV \end{aligned}$$

- Let us say that the infinitesimal change in volume has occurred because of a quasi-static reversible isothermal process during which the system draws $đq_R$ of energy in the form of (reversible) heat from the heat reservoir.
- We have $PdV = đq_R$, which implies that,

$$dS = \frac{Nk_B}{PV}\ đq_R$$

- Replace PV by Nk_BT (ideal gas law which we have already derived) in the above expression.

- We get,

  $$dS = \frac{đ q_R}{T}$$

  which is precisely the definition for change in entropy given by Clausius.
- Thus Clausius' entropy readily follows from Boltzmann's entropy.
- Boltzmann gives an expression for the absolute entropy. Clausius gives an expression for change in entropy.
- Both Boltzmann entropy and Clausius' entropy are defined for an equilibrium system.

Gibbs' paradox

- We derived all the above expressions starting from the following,

$$\hat{\Omega} = V^N; \; S = Nk_B \log V$$

  - Is this entropy extensive?
  - No; it is not: *Check this out*
  - called Gibbs' paradox.
  - What should we do to make it extensive ?
  - Divide $\hat{\Omega}$ by $N!$; the resulting entropy is extensive.
  - This was suggested by Boltzmann for taking care of *indistinguishability*.

- The correct full expression for $\hat{\Omega}$ as a function of U, V and N is given by the Sackur-Tetrode equation,

$$\hat{\Omega}(U,V,N) = V^N \frac{1}{h^{3N}} \frac{1}{N!} \left(\sqrt{2\pi m}\right)^{3N} \frac{U^{3N/2}}{\Gamma(\frac{3N}{2}+1)}$$

- h^{3N} is the (phase space volume) unit we use to measure the volume of the $6N$ dimensional phase space;
- this choice of unit volume is inspired by the Heisenberg uncertainty principle: $\Delta x \Delta p \ge h$
- We take the ' minimum uncertainty ' volume of the phase space, $\prod_{i=1}^{N} \prod_{k=1}^{3} \Delta x_i^{(k)} \Delta p_i^{(k)} = h^{3N}$
- $\Gamma(y)$ is the usual gamma function defined by, $\Gamma(y) = \int_0^\infty \exp(-x) x^{y-1} dx$; $\Gamma(\nu+1) = \nu\,!$

Boltzmann-Gibbs-Shanon Entropy

Josiah Wilard Gibbs (1839 - 1903)
Claude Elwood Shanon (1916 - 2001)

- Consider an isolated system; let Ω_{IS} denote the set of all possible microstates accessible to the system; let $\hat{\Omega}_{IS}$ denote the number of microstates.

$$\begin{aligned} S &= k_B \log \hat{\Omega}_{IS} \\ &= k_B \ \frac{1}{\hat{\Omega}_{IS}} \ \hat{\Omega}_{IS} \ \log \hat{\Omega}_{IS} \\ &= -k_B \sum_{i=1}^{\hat{\Omega}_{IS}} \frac{1}{\hat{\Omega}_{IS}} \ \log\left(\frac{1}{\hat{\Omega}_{IS}}\right) \end{aligned}$$

- This can be written in more suggestive form,

$$S = -k_B \sum_{i=1}^{\hat{\Omega}_{IS}} p_i \log p_i$$

where, $p_i = 1/\hat{\Omega}_{IS} \ \forall \ i$:

'*all microstates are equally probable* '

- We can generalize and say that the above gives an expression for entropy even when the probabilities are not the same for all microstates. thus we get the Boltzmann-Gibbs-Shanon entropy.

- For example consider a closed system;
- the system is in contact with a heat bath with which it exchanges only energy; it does not exchange matter;
- we get a canonical ensemble defined by a set of microstates Ω_{CS} and probabilities

  $$p(\mathcal{C}) = Z^{-1} \exp\left[-\beta E(\mathcal{C})\right].$$

  In the above $\mathcal{C} \in \Omega_{CS}$; Z is the normalization and is called the canonical partition function given by,

  $$Z(T, V, N) = \sum_{\mathcal{C}\in\Omega_{IS}} \exp\left[-\beta E(\mathcal{C})\right]$$

- For an open system, which exchanges energy as well as matter with the bath, we have Ω_{OS} denoting the set of all microstates; the probabilities are given by,

$$p(\mathcal{C}) = \mathcal{Q}^{-1} \exp\left[-\beta E(\mathcal{C}) + \beta\mu N(\mathcal{C}) \right]$$

- In the above $\mathcal{C} \in \Omega_{OS}$; μ is the chemical potential; $\mathcal{Q}$ is the grand-canonical partition function; $N(\mathcal{C})$ is the number of particles in the system when in microstate $\mathcal{C}$.

$$\mathcal{Q} = \sum_{\mathcal{C} \in \Omega_{OS}} \exp\left[-\beta E(\mathcal{C}) + \beta\mu N(\mathcal{C}) \right]$$

ϵ_j : energy of the microstate j

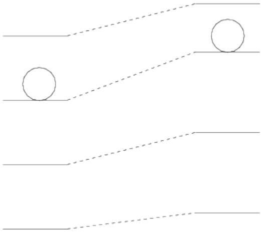
p_j : probability of the microstate j

$$\begin{aligned} U &= \sum_j p_j \epsilon_j \\ dU &= \sum_j \left[\frac{\partial U}{\partial p_j}\ dp_j + \frac{\partial U}{\partial \epsilon_j}\ d\epsilon_j \right] \\ &= \sum_j \left[\ \epsilon_j\ dp_j + p_j\ d\epsilon_j \ \right] \\ &= \sum_j \epsilon_j dp_j + \sum_j p_j d\epsilon_j \\ &= \quad đq \quad + \quad đW \end{aligned}$$

- $\sum_j \epsilon_j dp_j$ refers to Heat;
  - This term refers to the energy exchanged by the system with the heat bath in the form of heat.
  - during this process, the energy of a microstate does not change.
  - only the occupation probabilities $\{p_i\}$ change.
- $\sum_j p_j d\epsilon_j$ refers to Work done on the system.
  - during this process the occupation probabilities - $\{p_j\}$ do not change.
  - only the energy of the microstates change.
  - *e.g.* when we change volume (boundary conditions) the energy eigenvalues of the system change.

Work Term

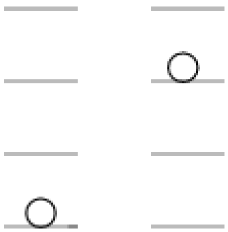
$$\left(\sum_j p_j d\epsilon_j \right)$$



- the system remains in the same microstate; only the energy of the microstate changes taking the system along with it.

$$
\begin{aligned}
\sum_j p_j d\epsilon_j &= \sum_j p_j \left(\frac{\partial \epsilon_j}{\partial V}\right)_{\{p_j\}} dV \\
&= \left(\frac{\partial}{\partial V}\sum_j p_j \epsilon_j\right)_{\{p_j\}} dV \\
&= \left(\frac{\partial U}{\partial V}\right)_{S,N} dV \\
&= -P\ dV
\end{aligned}
$$

Heat Term ($\sum_j \epsilon_j dp_j$)



- The energies of the microstates do not change; the energy put in (or extracted out) **in the form of heat** induces the system to make a transition from one microstate to another of higher (or lower) energy ; such a transition could occur even otherwise by a spontaneous fluctuation.

$$
\begin{aligned}
S = -k_B \sum_j p_j \log p_j ;\ \ dS &= -k_B \sum_j [dp_j + dp_j \log p_j] \\
\left[\sum_j dp_j = 0 \right] ;\ \ dS &= -k_B \sum_j dp_j \log p_j \\
\left[p_j = \exp[-\beta\epsilon_j]/Z \right] ; \qquad & \log p_j = -\beta\epsilon_j - \log Z \\
dS &= k_B \sum_j dp_j [\beta\epsilon_j + \log Z] \\
\left[\sum_j dp_j \log Z = 0 \right] \qquad & dS = k_B \beta \sum_j dp_j \epsilon_j ; \\
T dS &= \sum_j dp_j \epsilon_j = đ q_R
\end{aligned}
$$

- Consider an irreversal process in which we switch the value of a thermodynamic variable λ from $0 \rightarrow 1$
- We start the switching when the system is in equilpibrium with the surroundings at inverse temperature β.
- Let τ be the switching time
- during the switching process and a the end of the switching process the system need not be in equilibrium
- the system can go far from equilibrium
- Let $\{W_i \ : \ i = 1, N\}$ be the values of W observed in N N switching experiments, all carried out with the same protocol

- Work fluctuation theorem says, for experiments carried out with an irreversible protocol, we can

$$\frac{1}{N}\sum_{i=1}^{N}\exp(-\beta W) \quad = \quad \exp(-\beta\Delta F)$$

- on the left we have a quantity measured in a nonequilibrium process
- on the right we have an equilibrium quantity
- an equilibrium quantity can be obtained from measurements from irreversible processes
- this is a remarkable finding

- there are other equalities relating non-equilibrium measurements to equilibrium quantities based on
    - entropy and
    - heat fluctuations
- there are attempts to define entropy for nonequilibrium systems from Chaos theory
- some success has been obtained for steady state systems
- these constitute recent trends in thermodynamics
- these constitute recent developments in thermodynamics

- exponential is a convex function : $\langle e^{-x} \rangle \ > \ e^{\langle x \rangle}$
- we recover the second law inequality from work fluctuation theorem $\langle W \rangle > \Delta F$ for an irreversible process
- in the reversible limit $\tau \to \infty$ we recover conventional thermodynamics relation $\langle \ W \ \rangle = \Delta F$
- For τ large but not infinity, we get

$$\langle W \rangle - \Delta F = \frac{1}{2}\beta\sigma_W^2$$

dissipation is proportional to fluctuation

- Let

$$p = \int_{-\infty}^{W_R} \rho(W,\tau) dW$$

- in the above $\rho(W,\tau)$ describes the work ensemble of non-equilibrium experiments all carried out with the same protocol over time duration τ
- in the reversible limit there is no dissipation $W_d = 0$
- in the reversible limit we also have $\sigma^2_W = 0$
- Fluctuation dissipation theorem says

$$\sigma^2_W \propto W_d$$

- the above implies $\sigma_W \ >> \ W_d$
- after a bit of algebra we find that when the process becomes more and more reversible $p \to 1/2$
- p is the probability of second law violation at microscopic level
- the result that $p = 1/2$ in the reversible limit is paradoxial
- Is it that we have Maxwell's demon reborn ?
- these are open questions and we require fresh thinking from young minds

THANKS