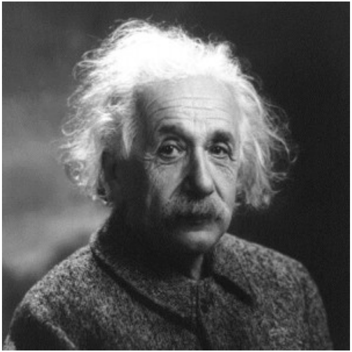
- **Thermo** : heat
- **dynamics** : motion

Thermodynamics is the study of motion of heat.

- Most thermodynamical variables depends on the **temperature** of the system.
- Although it is dynamics - one interesting aspect - **Time** however does not enter in most of the thermodynamic equations. Did you notice that **Temperature** did not enter in most of the equations in Mechanics, and will notice that it does not enter Quantum Mechanics and Electrodynamics equations !!
- Thermodynamics describes average properties (that generally does not depend on details of position/velocity) of macroscopic (matter that contains atoms or molecules) matter in equilibrium. Such as Volume, Pressure, Temperature (called as thermodynamic coordinates or variables or parameters).

- A state of macroscopic matter where average properties does not change with time - Equilibrium State (usually no external driving force exists).
- In thermodynamics, the average macroscopic properties of the system are not independent of each other. Measure a subset of properties and then calculate the remaining using thermodynamic relations.
- You will see that the laws (4 in number) of thermodynamics are **general**. They describe any system in equilibrium - a wide variety of physical and chemical systems.
- Thermodynamics was formulated in 18th and 19th Century - before we knew in detail the structure of matter. Hence it works even if matter constituents are not fully known.



Thermodynamics is the only physical theory of universal content which, within the framework of applicability of its basic concepts, I am convinced will never be overthrown.

TREATISE ON
THERMODYNAMICS

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I had no alternative but to tackle the problem again … from the side of thermodynamics. In fact, my previous studies of the Second Law of Thermodynamics came to stand me in good stead now, for at the very outset I hit upon the idea of correlating not the temperature of the oscillator but its entropy with the energy... While a host of outstanding physicists worked on the problem of the spectral energy distribution both from the experimental and theoretical aspect, every one of them directed his efforts solely towards exhibiting the dependence of the intensity of radiation on the temperature. On the other hand, I suspected that the fundamental connection lies in the dependence of entropy with the energy … Nobody paid any attention to the method which I adopted and I could work out by calculations completely at my leisure, with absolute thoroughness, without fear of interference or competition.

Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are used to it, it doesn't bother you anymore.

Drawbacks: Lots of abstract concepts to be learned before we get into interesting applications.

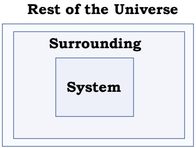
Usefulness of Thermodynamics

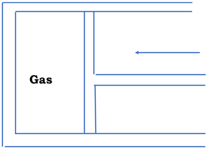
- How do engines and refrigerators work ? What are the physical limits on their performance ? Remember it was Steam Engine which brought the so called Industrial Revolution.
- How the products of a chemical reaction depends on temperature and pressure
- Why are there gases, liquids and solides? What are the laws governing transitions between these phases ? What happens when we mix different substances? Why alloys generally have lower melting temperatures than their constituents?
- Allows us to describe macroscopic property of a system in equilibrium by using a set of a few measurable quantities.

Microscopic

- Consider a macroscopic body - say a block of metal and suppose it has 10^{23} atoms.
- To predict its time evolution we need to solve 3×10^{23} equations of motion
- $M_i \frac{d^2 X_i}{dt^2} = - \frac{\partial V(X_i)}{\partial X_i}$
- The output is 3×10^{23} functions $X_i(t)$ which will describe the time evolution of the system.
- \- Looks impractical and also may give lots of not needed information.

- Take the same example of block of metal - In a macro world only macroscopic coordinates are relevant - Length, Height, Width etc
- 99.99% of its microscopic coordinates (position of atoms and their velocities) do not describe its macroscopic behaviour directly (although they are related).
- Later on we will club all these macroscopically **invisible** coordinates into a single variable/parameter that describes the internal degrees of freedom.
- Choice of thermodynamic variables is an art. For example number of particles in a macroscopic system is very large. We can make use of Mole - contains Avogadro's number of particles ($N_A = 6.02217 \times 10^{23}$); Number of particles in 12 grams of Carbon isotope 12^C; Mole number = Number of particles / N_A.





- Zone of interest is the **system** it interacts with the **surroundings**
- System and the surroundings are separated by a **boundary** wall. The boundary defines what is held constant in the system. For example, a moving piston means **volume** is not constant.
- A well insulated piston means no heat flow - **adiabatic**. No heat is allowed in and out of the system. Many times in this course we will be talking about adiabatic walls separating thermodynamic system. These walls do not allow heat transfer. Diathermal walls allow heat transfer.
- Slow compression with no insulation means the temperature is constant - **isothermal**
- In a thermodynamic process how system variables change depends on the surroundings.

There are two types of variables/parameters/coordinates in thermodynamics.

- **Extensive**: Values are proportional to the size of the system. Examples: Mass, Energy, Volume, Mole numbers, heat capacity
- **Intensive**: Values that do NOT depend on the size of the system. Example: Pressure, Temperature, Mole fraction, density, specific heat capacity

There could however be contraints on the extensive variables. For example: The number of gas molecules in a sealed bottle is **fixed**. That implies the number of moles are constrained. If we open the bottle the number of gas molecules within the bottle may change due to other parameters like the temperature or pressure - then the Mole numbers are not constrained.

Internal Energy

A macroscopic system possesses a well defined energy

- consists of kinetic energy of atoms/molecules in the rest frame of the centre of mass of the system + energy of interaction between atoms/molecules (internal potential energy).
- This is total energy is called **Internal Energy**.
- Denoted by U
- Total energy is defined up to an arbitrary constant. Hence only energy differences are physically meaningful.
- Internal energy is an extensive thermodynamic quantity.

- Thermodynamics is about MACROSCOPIC properties.
- The various properties that can be quantified without disturbing the system eg internal energy U and V, P, T are called state functions or state properties.
- Properties whose absolute values are easily measured eg. V,P,T are also called state variables.
- Relations between state functions for a particular system are called the equation of state of the system.
- Ideal gas: PV=NRT

Zeroth Law:

If each of two systems is in thermal equilibrium with a third system they are in thermal equilibrium with each other.

The argument can be repeated for fourth,fifth, ... systems (D, E, ...).
If each is in thermal equilibrium with all the others, they must have the same value of some property that has a common value.
This property is called thermodynamic temperature T.
The direction of heat flow tells us which system is at higher temperature.
Thermodynamic equilibrium temperature gives an ordering from cold to hot, and defines "equal temperature" but is not a numerical scale.

If many systems are in thermal equilibrium with each other, they must have the same value of some property (state variable). This property is called the thermodynamic temperature T.
The temperature of a system is a property that determines whether or not that system would be in thermal equilibrium with other systems.
For two systems to be in complete thermodynamic equilibrium, they must have a com- mon temperature and show no net (1) exchange of material (no difusion), (2) chemical reaction (chemical equilibrium), (3) unbalanced force (mechanical equilibrium) (4) charge flow (electromagnetic equilibrium).

Empirical observation of Gas Laws leads to a temperature scale...
$T = PV/nR$
The value of temperature is in Kelvin, which is denoted by K.
From kinetic theory of gases we have the temperature which connects to microscopic kinetic energy.
Remarkably, the Temperature related to the kinetic energy of an ideal gas, the Temperature which determines thermal equilibrium, and the Temperature which appear in statistical distributions (Boltzmann, Fermi-Dirac and Bose-Einstein) are all the same.
BTW: To relate Kelvins to Joules requires an accurate measurement of Boltzmann constant, e.g. from the speed of sound in ideal gas. Please look at A low-uncertainty measurement of the Boltzmann constant, Michael de Podesta et al., Metrologia, 50 (2013) 354 : https://iopscience.iop.org/article/10.1088/0026-1394/50/4/354 - Suggest discuss in Tutorial.