Thermodynamics Lecture Notes: Chapter 1

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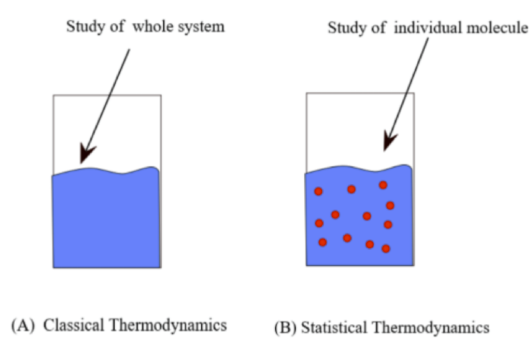
1 Introduction

1.1 What is Thermodynamics?

- Thermodynamics is a **branch of physics that deals with the relationships between heat and other forms of energy.**
  - how is energy transferred in systems and how can these energy transformations do work?
  - what is the specific role of thermal energy?
  - what causes certain transformations to occur spontaneously, but we never see the reverse happen?
- Thermodynamics has wide-ranging **applications**, including in engineering, chemistry, biology, and atmospheric science $\rightarrow$ understanding phenomena in engines, refrigerators, stars, and the Earth's climate
- Predicts: Is a physical/chemical reaction/process spontaneous and what happens during its evolution? How can a process be optimised to achieve a maximally useful effect?
- We distinguish between classical thermodynamics (macro variables like P, T, V) and statistical thermodynamics (statistical properties of individual particles, i.e. their velocity).



1.2 A bit of history

Early foundations in the 17-18th century:
From very early on, physicists have focused on the problem of measuring temperature, which is much more difficult to do universally than measuring lengths or masses, for example.

By the end of the 18th century, heat was considered a fluid (called caloric). This theory was plausible except for phase changes and the "creation" of caloric from work $\rightarrow$ experiments of H. Davy in 1799 are beginning of the end of the idea of a caloric fluid.

1824: Sadi Carnot, a French physicist, published "Reflections on the Motive Power of Fire," a treatise that laid the groundwork for the second law of thermodynamics. He analyzed the efficiency of steam engines and proposed a theoretical model, the Carnot cycle, which is still fundamental in thermodynamics.

1840s-1850s: The first law of thermodynamics, the conservation of energy, was formulated by Julius Robert von Mayer, James Prescott Joule, and Hermann Helmholtz. They showed that both heat and mechanical work are forms of energy and can be converted into each other.

Specifically, in 1847, Helmholtz stated the first principle (23 years after the second): "Energy can only be transferred from one form to another".

1860s: Rudolf Clausius re-formulated the modern version of the second law of thermodynamics Impossibility of building a machine that fully converts heat into work, with concepts like entropy and irreversible processes. This initiated the microscopic theory of heat and microscopic definition of entropy.

Statistical Thermodynamics (Late 19th Century):
Ludwig Boltzmann and James Clerk Maxwell developed statistical mechanics, bridging the microscopic behavior of atoms and molecules with the macroscopic laws of thermodynamics. Deriving the conservation laws from Noethers theorem is crucial in understanding the microscopic behavior of TD systems

Third Law (Early 20th Century):
The third law of thermodynamics, concerning the entropy of a system at absolute zero temperature, was developed by Walther Nernst between 1906-1912.

Expansion and Applications (20th Century):
Throughout the 20th century, the principles of thermodynamics found applications in a variety of new fields.

1.3 Forms of Matter

Three phases of matter: gas, liquid and solid. For water: vapour - boiling point - water - freezing point or melting point - ice

- **From macroscopic point of view:**
  - solid: maintains a fixed shape and a fixed size even if a large force is applied
  - liquid: does not maintain a fixed shape (takes a shape of the container), but not compressible
  - gas: has neither fixed shape nor volume, expands and fills the container
- **From microscopic point of view:**
  - Solid: The force between the particles (atoms or molecules) is strong enough that they cannot move free and can only vibrate.

- Liquid:Atoms have many nearest neighbours in contact, yet no long-range order is present.
- Gas: In a gas, the molecules have enough kinetic energy so that the effect of intermolecular forces is small (or zero for an ideal gas), and the typical distance between neighboring molecules is much greater than the molecular size.

Some general notations:

- Molecule - Atom - Nucleus (protons and neutrons) and electrons
- Atomic number (Z) and Mass number (A)
- Z = number of proton, A = number of nucleons (protons plus neutrons)
- Unified atomic mass unit (u): mass of $^{12}C = 12u$ where ($1u = 1.6605 \times 10^{-27}$kg) ^{12}C: 6 protons and 6 neutrons, i.e. one proton or neutron $\approx$ 1 u

Typical size of atom $\sim 10^{-10}$m - How can we estimate this?

- Cupper (solid) density = 8.9×10^3 kg/m^3
- Mass of one Cu atom = 62.930 u = $62.930 \times 1.661 \times 10^{-27}$ kg = 1.045×10^{-25} kg
- The number of Cu atoms per 1m^3 = $\frac{\text{density of Cu}}{\text{weight of Cu atom}} = \frac{8.9\times 10^3 \text{kg/m}^3}{1.045\times 10^{-25}\text{kg/atom}} = 8.5 \times 10^{28}$
- The number of atoms along one dimension n
- The number of atoms in a cube $N = n^3$
- For 1m x 1m x 1m: $n = N^{1/3} = (8.5 \times 10^{28})^{1/3} = 4.4 \times 10^9$
- The distance between atoms = $\frac{\text{distance}}{\text{number of atoms}} = \frac{1\text{m}}{4.4\times 10^9\text{atoms}} = 2.3 \times 10^{-10}$m.

Indicating that the distance between the atoms in a solid is close to the size of the atom.

What are the distances between atoms/molecules in gas (e.g. Oxygen at 0° C)?

- Oxygen gas density at 0° with the normal pressure = 1.429 kg/m^3
- Weight of one atom = 15.999 u = $15.999 \times 1.661 \times 10^{-27}$ kg = 2.657×10^{-26} kg
- The number of O atoms per 1 m^3 = density of O / weight of O atom = $\frac{1.429\times \text{kg/m}^3}{2.657\times 10^{-26}\text{kg/atom}}$ = 5.4×10^{25}.
- The number of atom along one dimension: $n \rightarrow$ The total number of atoms in a cube: $N = n^3 \rightarrow n = N^{1/3} = (5.4 \times 10^{25})^{1/3} = 3.8 \times 10^8$
- The distance between atoms = $\frac{\text{distance}}{\text{number of atoms}} = \frac{1\text{m}}{3.8\times 10^8\text{atoms}} = 2.3 \times 10^{-9}$m.

Distance between the atoms in a gas is about an order of magnitude larger than the size of the atom.