

Thermodynamics – Lecture 1 Aims

- To introduce the course;
- To give an overview of the syllabus and provide a motivation for studying this important topic;
- To introduce the correct terminology for describing thermodynamics;
- To re-cap the zeroth Law of thermodynamics and temperature.

1. Motivation

Second law of central importance in science – why changes occur.
 Not only the basis for why engines run/chemical reactions happen; it also tells us the why, foundation of the chemical reaction consequences (thoughts, creativity – music, drama, physics...)

Classical thermo – looks at a few basic bulk properties of materials, and their behaviour (Macroscopic picture). Quite general + no why.
 Emerged before atoms, when atoms discovered people realised could describe the microscopic picture, very detailed (1 mole $\sim 10^{24}$ atoms)
 Need to treat statistically.

2. Overview

Subject came about in 19th Century – engineers wanted to develop efficient machines – convert heat to work. Statistical mechanics developed (Boltzmann + Gibbs) took at underlying molecular interpretation, much richer understanding.

Example 2.1 : Lecture theatre $\sim 3 \times 10^6$ litres of air
 $(20 \times 10 \times 15) \text{ m}^3 \sim 10^{24}$ molecules

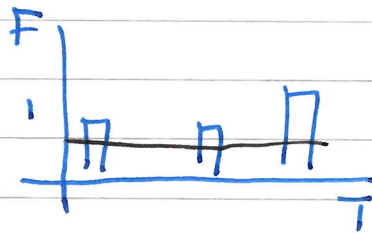
Count using 10GHz processor, 1 molecule/cycle, count 3×10^{17} molecules/year \Rightarrow Average desktop 3×10^{11} yrs to count all molecules $> T_H \sim 10^{10}$ yrs

In thermal equilibrium, most atoms behave as average, with no small scale fluctuations. As atoms increases, average is constant and fluctuations smooth \rightarrow thermodynamic limit

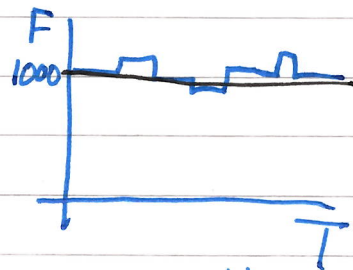
particles $\rightarrow \infty$, thermo behaviour asymptotically approaches approximated by Statistical Mechanics. Material properties are constant

Example 2.2 Consider hitting roof of various sizes

Small, odd droplets hit \rightarrow impulse



Large roof Many drops hit



Higher force on large roof, less fluctuation. Average smooths

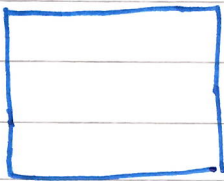
pressure = $\frac{\text{Force}}{\text{Area}}$, for both roofs — the same

As area $\rightarrow \infty$ $p \rightarrow p_0$, thermodynamic limit

Example 2.3 Definition of terms

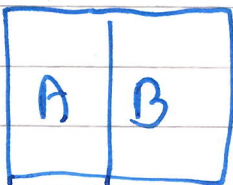
Extensive - System Extent

Intensive - Independent of size



Volume, V
Internal Energy, U

Temperature, T
pressure, p

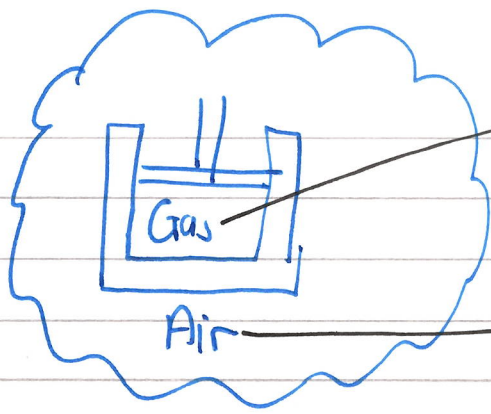


$V^\# = V_A = V_B = V/2$
 $U^\# = U_A = U_B = U/2$

$T^\# = T_A = T_B = T$
 $p^\# = p_A = p_B = p$

System properties related by an equation of state
 $f(p, V, T, U) = 0$

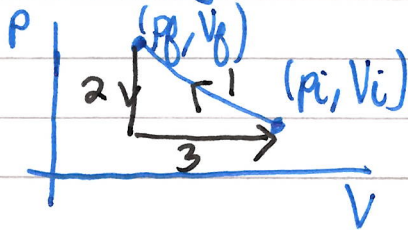
Ideal gas $pV = RT$, $pV - RT = 0$



System. Move piston the boundary changes

Surroundings

Change boundary, system state changes along path.
Shut piston, volume decreases (at constant temperature)
so pressure increases



System changes along path

1 → 2 → 3 returns to our initial state.

3. Thermal Equilibrium, Heat + Temperature

Heat is energy in transit — Can add heat, but can't say object contains a quantity of heat

Heat moves (spontaneously) from hot to cold — energy must be supplied to move heat cold → hot.

Thermal equilibrium — no heat transfer.

Example 3.1 Prepare a gas, a range of pressures / volumes

$$p_1 V_1 = a > b = p_2 V_2$$

Empirically find sample 1 is hotter
 $pV = f(T)$, equation of state.

Heat capacity — the amount that must be supplied / removed to change an object's temperature

$$\Delta Q = mc \Delta T$$

A small change dT in an object's temperature requires the addition/removal of a differential amount of heat δQ

Heat capacity, Capital C [whole object]
Specific heat capacity, lower case c [per unit mass (mole)]
 $C = mc$

How much heat is required to change an object's temp $T_1 \rightarrow T_2$?

$$\Delta Q = \int \delta Q = \int_{T_1}^{T_2} C dT = C(T_2 - T_1)$$

If C is independent of temperature

Most changes happen when some condition is constant
(volume, pressure)

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V, \quad C_P = \left(\frac{\partial Q}{\partial T} \right)_P$$

4. Zeroth Law - Establishes Temperature

Two bodies at same temperature, in thermal equilibrium
Heat goes hot \rightarrow cold under action, irreversible, as
move to thermal equilibrium define an arrow of time

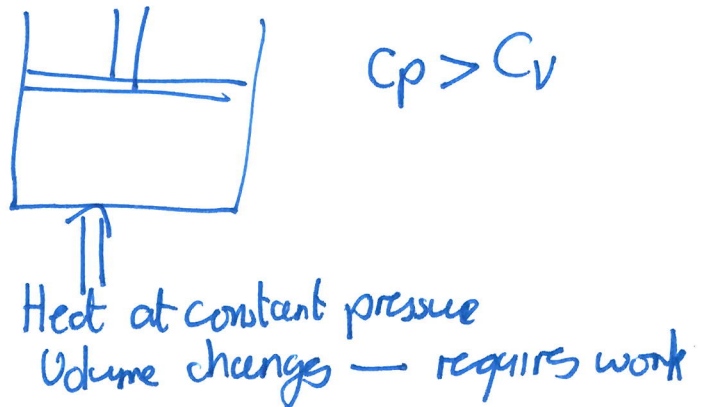
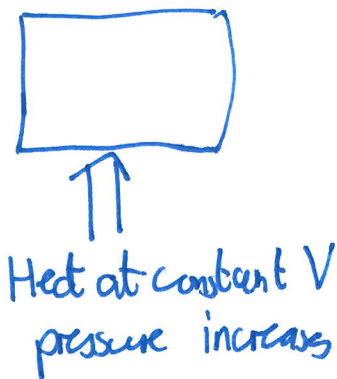
If two bodies are separately in thermal equilibrium with a
third body, the original two bodies must be in thermal
equilibrium with each other.

Thermodynamics – Handout 1

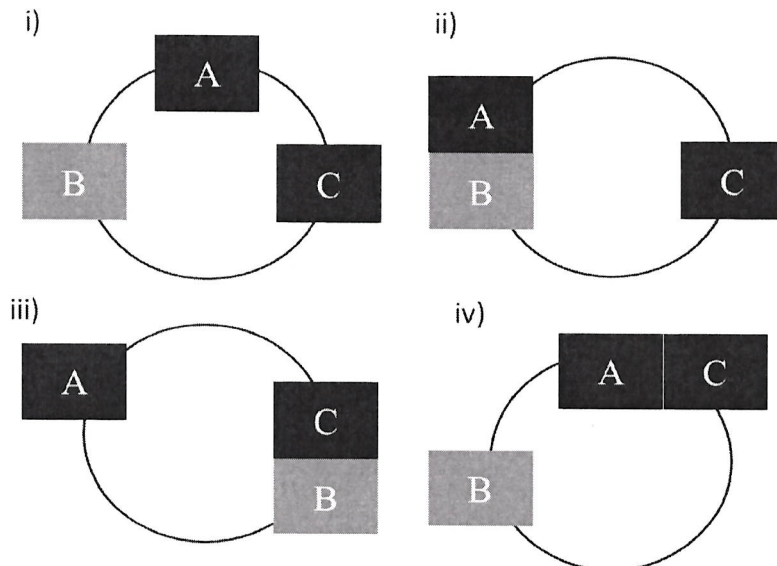
Exercise 1

Which is bigger, the heat capacity at constant pressure, C_p or the heat capacity at constant volume, C_V ?

- 1) Heat capacity at constant pressure is larger: $C_p > C_V$.
- 2) All heat capacities are equal: $C_p = C_V$.
- 3) Heat capacity at constant volume is larger: $C_V > C_p$



Zeroth Law of Thermodynamics



B is the thermometer

Put A in contact with B,
and B takes some value (ii)

Put C in contact with B
and value of B doesn't change
(iii)

A and C must be in thermal
equilibrium without doing
the experiment (iv)

Figure 1: Representation of the Zeroth Law of Thermodynamics.

And Law gives temperature scale.