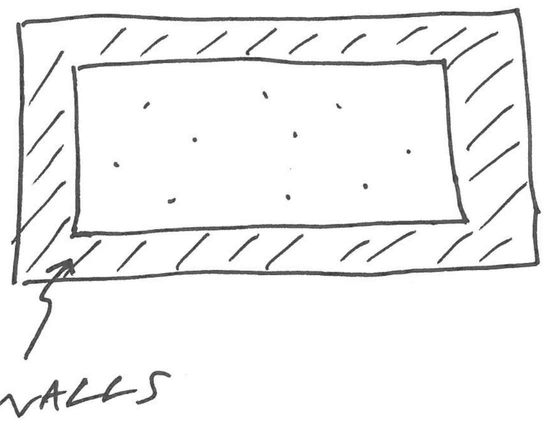
INTRODUCTION

- THIS SUBJECT IS CALLED **STATISTICAL MECHANICS** (STAT MECH)

- CONSIDER A BOX OF GAS



AT EQUILIBRIUM THE MACROSCOPIC STATE ("MACROSTATE") IS CHARACTERISED BY

- PRESSURE = p (Pa)
- VOLUME = V (m^3)
- TEMP = T (K)
- AMOUNT = No. OF MOLES = ν (mol)
- INTERNAL ENERGY = E (J)
- ENTROPY = S (JK^{-1})

THERMODYNAMICS : DESCRIBES THE BEHAVIOR OF MACROSCOPIC SYSTEMS IN TERMS OF A FEW PARAMETERS (eg $p, V, \nu, T, E, \ldots$)

- THERMAL EQUILIBRIUM : ALL MACRO PARAMETERS ARE TIME INDEPENDENT
- TEMP & ENTROPY PLAY A FUNDAMENTAL ROLE BUT ARE MYSTERIOUS.

STAT MECH : AIMS TO PROVIDE AN "EXPLANATION" OF THERMODYNAMICS IN TERMS OF MICROSCOPIC DEGREES OF FREEDOM (DoF).

MECHANICS ~ MEANS: RELATING TO PARTICLES
STATISTICAL ~ REFERS TO THE MANNER IN WHICH RAPID FLUCTUATIONS OF MICROSCOPIC VARIABLES ARE AVERAGED TO ARRIVE AT A MACROSCOPIC DESCRIPTION.

EQUILIBRIUM THERMODYNAMIC STATES

- IN THIS COURSE WE WILL ONLY BE INTERESTED IN EQUILIBRIUM THERMODYNAMICS

- A SYSTEM IN EQUILIBRIUM THERMODYNAMICS IS CHARACTERISED ONLY BY A FEW MACROSCOPIC PARAMETERS WHICH ARE TIME INDEPENDENT (eg p, V, T, etc)

- A MACROSCOPIC EQUILIBRIUM STATE IS COMPLETELY CHARACTERISED BY THE VALUES OF JUST SOME OF THE MACROSCOPIC PARAMETERS. FOR SYSTEMS WITH NO ELECTRIC OR MAGNETIC PROPERTIES ONE POSSIBLE CHOICE IS :

$$\boxed{E, \quad V, \quad \nu_1, \nu_2, \nu_3, \dots, \nu_n}$$

INTERNAL ENERGY

VOLUME

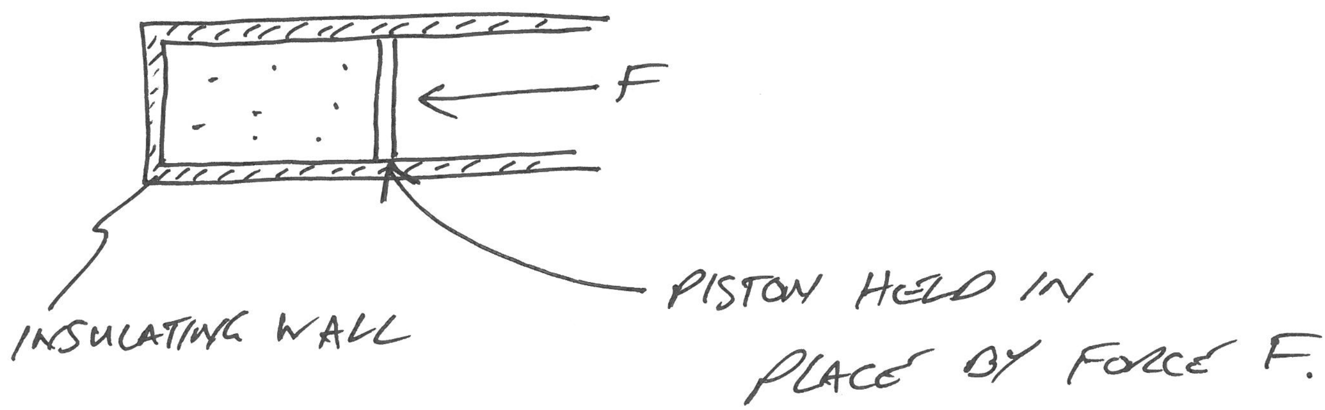
ν_i = No. OF MOLES OF CHEMICAL SPECIES i

- FOR A GIVEN <u>MACROSTATE</u> (ie FOR A SYSTEM WITH A GIVEN SET OF MACROSCOPIC VARIABLES E, V, ν_i) THERE ARE <u>MANY</u> POSSIBLE "MICROSTATES" (ie MANY MICROSCOPIC ARRANGEMENTS CONSISTENT WITH E, V, ν_i) & THE SYSTEM RAPIDLY TRANSITIONS OR "VISITS" THEM ALL.

- AN EQUILIBRIUM STATE IS INDEPENDENT OF ITS PAST HISTORY (SINCE IT DEPENDS ONLY ON E, V, ν_i).

- WHETHER OR NOT A SYSTEM IS IN AN EQUILIBRIUM STATE DEPENDS ON THE "CONSTRAINTS" THAT ARE APPLIED.

<u>EXAMPLE</u>: A CYLINDER OF GAS IN EQUIL.



- REMOVE THE FORCE — THE VOLUME CONSTRAINT HAS BEEN REMOVED & THE GAS IS NO LONGER IN EQUIL.

EQUATIONS OF STATE

- GIVEN A SYSTEM IN EQUILIBRIUM WITH GIVEN MACROSCOPIC VARIABLES

$$E, V, \nu_i, p, T, \ldots$$

NOT ALL ARE INDEPENDENT, AND THERE EXISTS <u>EQUATIONS OF STATE</u> WHICH RELATE THEM.

$\Longrightarrow$ THERE ARE MANY POSSIBLE CHOICES OF A MINIMAL (INDEPENDENT SET) OF VARIABLES WHICH FULLY CHARACTERISE THE EQUILIBRIUM STATE

EXAMPLES OF POSSIBLE INDEPENDENT SETS

- E, V, ν_i
- T, V, ν_i
- T, p, ν_i

EXAMPLES OF EQUATIONS OF STATE

• <u>IDEAL GAS</u>: THE EQUATIONS OF STATE ARE

$$\boxed{pV = \nu RT} \quad \text{—(1)}$$

$$\boxed{E = \alpha \nu RT} \quad \text{—(2)}$$

$$\alpha = \begin{cases} \frac{3}{2} & \text{MONATOMIC GAS} \\ \frac{5}{2} & \text{DIATOMIC GAS} \\ \frac{6}{2} & \text{POLYATOMIC GAS} \end{cases}$$

$$\boxed{\alpha = \frac{\text{No}^\circ \text{ OF DoF}}{2}}$$

(1) IS ALSO WRITTEN AS

$$pV = Nk_B T$$

k_B = BOLTZMANN'S CONST

N = No° OF GAS PARTICLES