RECAP

STATISTICAL MECHANICS

- FOR A SYSTEM IN A GIVEN MACROSCOPIC EQUILIBRIUM STATE (MACROSTATE) WITH GIVEN MACROSCOPIC PARAMETERS (p, V, T etc), THERE ARE MANY POSSIBLE MICROSCOPIC ARRANGEMENTS OF SYSTEM'S PARTICLES (i.e. MANY ACCESSIBLE MICROSTATES).

- WE LABEL EACH OF THE ACCESSIBLE MICROSTATES WITH AN INTEGER n

$$n = 1, 2, 3, \ldots$$

- FROM A QUANTUM MECHANICAL POINT OF VIEW, THE INTEGER n LABELS EACH OF THE ENERGY E' STATES ACCESSIBLE TO THE SYSTEM CONSISTENT WITH THE GIVEN MACROSTATE.

- THE CENTRAL PROBLEM OF STATISTICAL MECHANICS IS TO DETERMINE THE PROBABILITY $P_n^{(eq)}$ THAT AT A GIVEN INSTANT THE SYSTEM WILL BE IN THE STATE n.

$\{ P_n^{(eq)} : n = 1, 2, 3, \ldots \}$ — EQUILIBRIUM PROBABILITY DISTRIBUTION

STATISTICAL MECHANICS

- CONSIDER THE FOLLOWING "TOY MODEL" TO DEVELOPE THE IDEAS OF STAT MECH.

- GIVEN A SYSTEM IN A SPECIFIC <u>MACROSTATE</u> SUPPOSE THE <u>ACCESSIBLE MICROSTATES</u> (IE THE ALLOWED ENERGY E' STATES CONSISTENT WITH THE GIVEN MACROSTATE) ARE GIVEN BY

LABEL OF STATE	SYSTEM'S ENERGY STATES	ENERGY OF STATE	PROBABILITY OF STATE IN EQUIL
$n=4$		E_4	$P_4^{(eq)}$
$n=3$		E_3	$P_3^{(eq)}$
$n=2$		E_2	$P_2^{(eq)}$
$n=1$		E_1	$P_1^{(eq)}$

WE REQUIRE THAT

(i) $P_n^{(eq)}$ ARE TIME-INDEPENDENT

(AT EQUILIBRIUM THE PROBABILITIES OF EACH OF THE STATES SHOULD NOT CHANGE)

(ii) $\sum_{n=1}^{4} P_n^{(eq)} = 1$

IF THE ENERGY OF THIS SYSTEM IS MEASURED IT WOULD TURN OUT TO BE THE AVERAGE:

$$\bar{E} = E_1 P_1^{(eq)} + E_2 P_2^{(eq)} + E_3 P_3^{(eq)} + E_4 P_4^{(eq)}$$

$$\bar{E} = \sum_{n=1}^{4} E_n P_n^{(eq)}$$

THE FUNDAMENTAL POSTULATES OF STAT MECH

- GIVEN A SYSTEM IN A PARTICULAR MACROSTATE, LET $n = 1, 2, 3, \ldots$ LABEL THE ACCESSIBLE MICROSTATES (IE THE STATES CONSISTENT WITH THE GIVEN MACROSTATE)

- LET $\{P_n\}$ $n = 1, 2, 3, \ldots$ BE AN <u>ARBITRARY</u> PROBABILITY DISTRIBUTION OVER THE MICROSTATES. THE <u>GENERALISED ENTROPY</u> $\tilde{S}$ IS DEFINED AS FOLLOWS

$$\boxed{\tilde{S}(\{P_n\}) := -k_B \sum_n P_n \ln P_n}$$

<u>POSTULATE</u>: THE ACTUAL PROBABILITY DISTRIBUTION AT EQUILIBRIUM $\{P_n^{(eq)}\}$ IS THE ONE WHICH MAXIMISES $\tilde{S}$

i.e. $\tilde{S}(\{P_n^{(eq)}\})$ IS THE MAXIMUM POSSIBLE VALUE FOR ANY PROBABILITY DISTRIBUTION $\{P_n\}$.

FURTHERMORE $\tilde{S}(\{P_n^{(eq)}\})$ IS THE USUAL THERMODYNAMIC ENTROPY $S(E, V, \vec{N})$

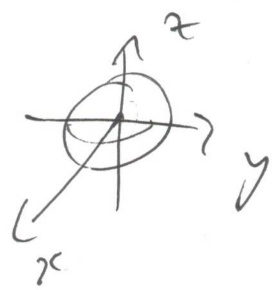
METHOD OF LAGRANGE MULTIPLIERS

EXAMPLE

SUPPOSE WE WISH TO EXTREMISE THE FUNCTION

$$\boxed{f(x,y,z) = x + y + z} \quad (1)$$

ON THE UNIT SPHERE



$$x^2 + y^2 + z^2 = 1$$

i.e WE WISH TO EXTREMISE (1) SUBJECT TO THE CONSTRAINT

$$\boxed{g(x,y,z) = x^2 + y^2 + z^2 - 1 = 0}$$

USING THE METHOD OF LAGRANGE MULTIPLIERS (2

WE EXTRIMISE

$$F(x,y,z) = f(x,y,z) - \lambda g(x,y,z)$$

TREATING x, y & z AS INDEPENDENT.

ie

$$\boxed{F(x,y,z) = x + y + z - \lambda\left(x^2 + y^2 + z^2 - 1\right)}$$

SO WE MUST SOLVE

$$\boxed{\begin{gathered} \frac{\partial F(x,y,z)}{\partial x} = 0 \\ \frac{\partial F(x,y,z)}{\partial y} = 0 \\ \frac{\partial F(x,y,z)}{\partial z} = 0 \end{gathered}}$$

So

$$\frac{\partial F}{\partial x} = 1 - 2\lambda x = 0 \quad \Longrightarrow \quad \boxed{x = \frac{1}{2\lambda}} \text{ (A)}$$

$$\frac{\partial F}{\partial y} = 1 - 2\lambda y = 0 \quad \Longrightarrow \quad \boxed{y = \frac{1}{2\lambda}} \text{ (B)}$$

$$\frac{\partial F}{\partial z} = 1 - 2\lambda z = 0 \quad \Longrightarrow \quad \boxed{z = \frac{1}{2\lambda}} \text{ (C)}$$

USING $x^2 + y^2 + z^2 = 1$ WE CAN NOW FIND λ USING (A), (B) & (C)

$$x^2 + y^2 + z^2 = 1$$

$$\Rightarrow \left(\frac{1}{2\lambda}\right)^2 + \left(\frac{1}{2\lambda}\right)^2 + \left(\frac{1}{2\lambda}\right)^2 = 1$$

$$\Rightarrow \frac{3}{4\lambda^2} = 1$$

$$\Longrightarrow \quad \lambda^2 = \frac{3}{4}$$

$$\Longrightarrow \quad \lambda = \pm \frac{\sqrt{3}}{2}$$

INSERTING $\lambda = +\sqrt{3}/2$ INTO (A), (B) & (C) GIVES

$$(x, y, z) = \left(\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}} \right)$$

& INSERTING THIS INTO $f(x, y, z)$ GIVES THE EXTREME VALUE

$$f\left(\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}} \right) = \frac{1}{\sqrt{3}} + \frac{1}{\sqrt{3}} + \frac{1}{\sqrt{3}} = \frac{3}{\sqrt{3}}$$

$$= \sqrt{3}$$

SIMILARLY, INSERTING $\lambda = -\sqrt{3}/2$ INTO

(A), (B) & (C) GIVES

$$(x, y, z) = \left(\frac{-1}{\sqrt{3}}, \frac{-1}{\sqrt{3}}, \frac{-1}{\sqrt{3}} \right)$$

& INSERTING THIS INTO $f(x, y, z)$ GIVES

THE EXTREME VALUE

$$f\left(-\frac{1}{\sqrt{3}}, -\frac{1}{\sqrt{3}}, \frac{-1}{\sqrt{3}}\right) = -\frac{3}{\sqrt{3}} = -\sqrt{3}$$