THE DISTRIBUTION FUNCTION $\{P_n^{(eq)}\}$ FOR AN ISOLATED SYSTEM

- CONSIDER AN ISOLATED SYSTEM WITH FIXED $E, V, \vec{N}$, AND LET $n = 1, 2, 3 \ldots$ LABEL THE ACCESSIBLE MICROSTATES CONSISTENT WITH THE GIVEN $E, V, \vec{N}$ VALUES. [NOTICE THAT THE ENERGY E_n OF EACH OF THESE STATES MUST BE $E_n = E$.]

- THE EQUILIBRIUM PROBABILITY DISTRIBUTION $\{P_n^{(eq)}\}$ WILL BE THAT WHICH MAXIMISES

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

WITH THE SUM OVER ALL STATES n COMPATIBLE WITH THE GIVEN $E, V, \vec{N}$

SO: WE HAVE TO MAXIMISE $\tilde{S}(\{P_n\})$

OVER ALL POSSIBLE ASSIGNMENTS OF

PROBABILITIES $\{P_n : n = 1, 2, 3, \dots\}$ SUBJECT

TO THE CONSTRAINT

$$\boxed{\sum_n P_n - 1 = 0}$$

INVOKE THE METHOD OF LAGRANGE MULTIPLIERS

– IT SUFFICES TO MAXIMISE

$$F(\{P_n\}) = -k_B \sum_n P_n \ln P_n - \lambda \left(\sum_n P_n - 1 \right)$$

LAGRANGE MULTIPLIER (A CONSTANT)

ie $$0 = \frac{\partial F(\{P_n\})}{\partial P_m}$$ m FIXED

$m = 1, 2, \dots$

$$\Rightarrow \quad 0 = \frac{\partial}{\partial P_m}\left(-k_B \sum_n P_n \ln P_n - \lambda\left(\sum_n P_n - 1\right)\right)$$

$$= -k_B \ln P_m - k_B \frac{P_m}{P_m} - \lambda$$

$$= -k_B \ln P_m - k_B - \lambda$$

$$\Rightarrow \quad \ln P_m = -\frac{(\lambda + k_B)}{k_B} = -\left(1 + \frac{\lambda}{k_B}\right)$$

$$\Rightarrow \quad \boxed{P_m^{(eq)} = e^{-(1 + \lambda/k_B)}} \qquad m = 1, 2, 3, \ldots$$

A CONSTANT

SET OF PROBABILITIES THAT MAXIMISE $\tilde{S}$

<u>FOR ISOLATED SYSTEMS</u>: ALL ACCESSIBLE ENERGY E'STATES (ie STATES COMPATIBLE WITH THE ENERGY E) ARE EQUALLY LIKELY TO BE OCCUPIED AT EQUILIBRIUM.

NOTE: SOME APPROACHES TO STAT MECH TAKE THIS AS AN AXIOM.

THIS MAKE SENSE: SYSTEMS "LIKE" TO MINIMISE THEIR ENERGY & HERE ALL ACCESSIBLE E'STATES HAVE THE SAME ENERGY $\Rightarrow$ ALL EQUALLY LIKELY.

DETERMINING λ: IMPOSE THE CONSTRAINT

$$\sum_n P_n = 1$$

$$\Rightarrow \sum_n e^{-(1+\lambda/k_B)} = 1$$

$$\Rightarrow e^{-(1+\lambda/k_B)} \sum_n 1 = 1$$

SUMMING OVER ALL ACCESSIBLE STATES (ie TOTAL No° OF STATES)

$$\sum_n 1 = \Omega(E, V, \vec{N})$$

$\Omega(E, V, \vec{N})$ — THE NUMBER OF ENERGY EIGENSTATES WITH ENERGY E

SO $$e^{-(1+\lambda/k_B)} = \frac{1}{\Omega(E, V, \vec{N})}$$

SO $$\boxed{\rho_n^{(eq)} = \frac{1}{\Omega(E, N, \vec{V})}}$$

← THIS IS CALLED THE <u>MACROCANONICAL DISTRIBUTION FUNCTION</u>

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

$$S(E,V,\vec{N}) = -k_B \sum_n P_n^{(eq)} \ln P_n^{(eq)}$$

$$= -k_B \sum_n \frac{1}{\Omega(E,V,\vec{N})}\left((-1)\ln \Omega(E,V,\vec{N})\right)$$

$$= k_B \frac{1}{\Omega(E,V,\vec{N})} \ln \Omega(E,V,\vec{N}) \underbrace{\sum_n 1}_{\Omega(E,V,\vec{N})}$$

$$\Longrightarrow \quad \boxed{S(E,V,\vec{N}) = k_B \ln \Omega(E,V,\vec{N})} \quad (1)$$

SO FOR AN ISOLATED SYSTEM THE THERMODYNAMIC ENTROPY IS GIVEN BY (1). THE QUANTITY $\Omega(E,V,\vec{N})$ IS DETERMINED BY A QUANTUM MECHANICAL CALCULATION (ie WE NEED TO COUNT THE NUMBER OF ENERGY E STATES)

FROM THE EQUATIONS OF STATE WE CAN THEN DEDUCE T, p, μ_i

ie $\boxed{\frac{\partial S}{\partial E} = \frac{1}{T}}$, $\boxed{\frac{\partial S}{\partial V} = \frac{p}{T}}$, $\boxed{\frac{\partial S}{\partial N_i} = \frac{-\mu_i}{T}}$