

## I) RIGOROUS Derivation of

$$P_r = P(E_r) = \frac{1}{\Omega} = \frac{1}{\left( \begin{array}{l} \text{no. of} \\ \text{QUANTUM} \\ \text{states w/} \\ E_0 - \Delta E \leq E_r \leq E_0 + \Delta E \end{array} \right)}$$

= prob. density for  
Microcanonical  
distribution.

a) Assume ensemble of  $\tilde{N}$   
replica systems

b) THE ENERGY OF ANY GIVEN SYSTEM, say  
system  $r$ ,  $E_r$ , CAN BE MEASURED w/  
A <sup>given</sup> UNCERTAINTY OF  $\Delta E$ .

THUS, THE ACTUAL QUANTUM  
energy states that any  
given system can assume  
lie in the range:

$$E_0 - \Delta E \leq E_r \leq E_0 + \Delta E$$

Lucy 19 Sep 15

(2)

where  $E_0$  is the average (measured) energy of the system of interest.

c) so, we can use the same argument we used to get  $P_r = P(\text{or})$  for a canonical ensemble.

i)  $\tilde{E} = \sum n_r E_r$

$\tilde{N} = \sum n_r$

$n_r =$  no. of systems @ time  $t$  in quantum state  $r$

$n_r =$  distn set  $j$

ii) no. of ways of observing a given distn set  $\{n\}$

$\{n_1, n_2, n_3, \dots, n_m\}$  is given

by

$$W(\{n\}) = \frac{\tilde{N}!}{n_1! n_2! n_3! \dots n_m!}$$

iii) @ equil., the most probable distn set that we can observe,  $\{n^*\}$  is the one corresponding to MAX  $W$ :

lec. 19  
 sm 15 (3)

iv) so set

$$F(\epsilon_{n3}) = \ln W + B' [E - \sum n_r \epsilon_r] + \alpha' [\tilde{N} - \sum n_r]$$

v)  $\therefore$   $\alpha', B' = \text{Lagrange multipliers}$   
 $F(\epsilon_{n3}) = \tilde{N} \ln \tilde{N} - \tilde{N} - \sum [\tilde{n}_r \ln n_r - \tilde{n}_r] + B' [E - \sum n_r \epsilon_r] + \alpha' [\tilde{N} - \sum n_r]$   
 @ EQUILIBRIUM;

$$\frac{\partial F}{\partial n_r} = -\ln n_r - 1 - B' \epsilon_r - \alpha' = 0$$

$$r = 1, 2, 3, \dots, M$$

vi)  $\therefore n_r^* = A_0 e^{-B' \epsilon_r}$

$$\tilde{N} = \sum n_r^* \Rightarrow A_0 = \frac{1}{\sum e^{-B' \epsilon_r}}$$

$$\therefore P(\epsilon_r) = \frac{n_r^*}{\tilde{N}} = \frac{e^{-B' \epsilon_r}}{\sum e^{-B' \epsilon_r}}$$

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d)  $P(E_r) = \frac{n_r^*}{N} = \frac{\exp[-B(E_0 + E_r')]}{\sum_{r=1}^M \exp[-B(E_0 + E_r')]} \quad (4)$

$E_r'/E_0 \ll 1$   
 $r=1, 2, \dots, M$

$$= \frac{\exp(-BE_0) + O(E_r'/E_0)}{\sum_{r=1}^M [\exp(-BE_0) + \beta \exp(-BE_0)(E_r'/E_0)]}$$

$$= \frac{\exp(-BE_0)}{\sum_{r=1}^M \exp(-BE_0)} + O(E_r'/E_0)$$

$$= \frac{e^{-BE_0}}{e^{-BE_0} \sum_{r=1}^M 1} = \frac{1}{M}$$

∴  $P(E_r) = \frac{1}{M} + O(E_r'/E_0)$

$M = \text{max. index. of distbn set.} \quad \Delta E$   
E.N.B.

e) FINALLY, SHOW THAT  $M=R \equiv$   
NO OF QUANTUM STATES (FOR  
OUR SYSTEM OF INTEREST)  
LYING w/in the band  
 $E_0 - \Delta E \leq E_r \leq E_0 + \Delta E$

i) 1E show that  $S = -k \ln \langle P_r \rangle$   
(for a canonical or microcanonical ens.)

1)  $\langle \ln P_r \rangle = \langle \ln e^{-B E_r} \rangle - \langle \ln Q \rangle$

2)  $\langle \ln Q \rangle = \ln Q$  since  $Q =$  a fixed number for any given set of quantum states  $E_1, E_2, \dots$  and given  $B = 1/kT$ .

3)  $\langle \ln e^{-B E_r} \rangle = \langle -B E_r \rangle = -B \langle E_r \rangle = -B U$

4)  $\therefore \langle \ln P_r \rangle = -B U - \ln Q$

5) But, since  $A = -kT \ln Q$ ,  $= -B^{-1} \ln Q$   
THEN

$$\begin{aligned} \langle \ln P_r \rangle &= -B U + B A \\ &= R [-u + u - TS] \\ &= -B TS \\ &= -S/k \end{aligned}$$

$\therefore \boxed{S = -k \langle \ln P_r \rangle} \quad \checkmark \quad (5.1)$

ii) NEXT USE

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$$P_r = \frac{1}{M}$$

IN (5.1) :

$(Y_M = \text{fixed number})$

$$S = -k \langle \ln Y_M \rangle = -k \ln Y_M$$

or  $\boxed{S = +k \ln M} \quad (6.1)$

iii) Finally, From our previous work (i.e., Boltzmann's Law),

since  $\boxed{S = k \ln \Omega}$

then

$$\boxed{M = \Omega}$$

$\therefore$  Since

$$P(E_r) = \frac{1}{M} + O\left(\frac{E_r}{E_0}\right)$$

Then  $\left[ P(E_r) = \frac{1}{\Omega} + O\left(\frac{E_r}{E_0}\right) \right]$

end proof