Derrivation of the Boltzman distribution

suppose there are a bunch of elements arranged such that n_1 are in quantum state 1, n_2 are in quantum state 2 and n_i are in quantum state i.

The number of ways in which n elements can be arranged with n_i in each state i is

$$\frac{n!}{\prod_i n_i!}$$

call this the probability of a macroscopic state P. for example consider 3 elements, ABC These can be arranged into several macroscopic states:

MACRO-SCOPIC STATES
- ALL IN STATE 1
- ALL IN STATE 2
- ONE IN STATE 1 AND 2 IN STATE 2
- TWO in STATE 2 And 1. in STATE 2

for a simple two state system.

NOW THERE ARE three MICROSCOPIC ways to get for example ONE IN STATE 1 AND 2 in STATE 2

ie

STATE 1	STATE 2
AB	C
AC	B
BC	A

so the probability of this state is said to be 3. (The probability of any state is $3+3+1+1=8$)

now we wish to find, all all possible macroscopic states the most Probable. we however put several constraints on the macroscopic states.

fixed # of elements $n = \sum n_i$

fixed total energy $E = \sum n_i e_i$

so we look for a stationary value of P

ie $\delta P = 0$ or equivalently $\delta \ln P = 0$

$$\delta P = \underbrace{\delta \ln n!}_{=0,\ n = \text{const}} - \sum_i \delta \ln n_i!$$

now $\ln n! \sim n \ln n - n$ so

$$-\delta P = 0 = \sum_i \ln n_i \, \delta n_i$$

now the small perturbations δn_i are not arbitrary but rather are linked via the constraints. ie

$$\sum \delta n_i = 0$$
$$\sum e_i \, \delta n_i = 0$$

Lagrange multipliers can then be used to solve the prob. for arbitrary α, β its true that

$$\sum [\ln n_i + \alpha + \beta e_i] \delta n_i = 0$$

suppose we choose α, β so that for $i = 1$ and 2 [ ] is identically zero. Then all the other δn_i's are truly independent and we have therefore that each [ ] in the sum must be zero for $i > 2$

$$\ln n_i + \alpha + \beta e_i = 0$$

$$n_i = \exp[-\alpha - \beta e_i] = e^{-\alpha} e^{-\beta e_i}$$

now we need only determine α and β.

since $n = \sum n_i = \sum e^{-\alpha} e^{-\beta e_i}$, $e^{-\alpha} = n / \sum e^{-\beta e_i}$

since $E = \sum n_i e_i = \sum e^{-\alpha} e^{-\beta e_i} e_i = \dfrac{n \sum e_i e^{-\beta e_i}}{\sum e^{-\beta e_i}}$