Boltzmann Equation

ASTR 300B

The Boltzmann Equation give the distribution of states for a system with total energy E at a temperature T.

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} e^{-\Delta E_{21}/kT_{ex}}$$

$\Delta E_{21} = E_2 - E_1$

excitation temperature

Boltzmann's CONST
$k \simeq 1.381 \times 10^{-16}$ erg K^{-1}

Statistical weights (degeneracies of energy levels)

For instance, e^- with angular momentum ℓ have $g = (2\ell + 1)$

We shall now derive this expression.

ASSUME (1) Total Energy CONSTANT

$$E = \sum_i n_i \varepsilon_i \qquad n_i = \text{number of particles with energy } \varepsilon_i$$

(2) Total number of particles is CONSTANT (AND LARGE)

$$N = \sum_i n_i$$

(3.) Particles are distinguishable (NOTE this may not be the case for some quantum gases)

We are going to analyze the "macrostate" Ω of a "microcanonical ensemble" of particles with energies ε_i

What the heck does that mean?? Lets use an example to derive the possible Combinations:

Assume you have 3 CONTAINER (A state that the particle can be put into) that hold the first 9 letters of the alphabet:

a b c d e f g h i

|_ _| |_ _ _| |_ _ _ _|

For the 1st slot, there are 9 possibilities — |c _| |_ _ _|
For the 2nd slot, there are 8 possibilities — |c h| |_ _ _|
For the 3rd slot, there are 7 possibilities — |c h| |b _ _|
etc.

$\Rightarrow$ there are 9! possible arrangements <u>if</u> the containers are ignored.

<u>BUT</u>, containers matter! We don't care about the ordering of letters within the container, so we divide out by the arrangement possibilities within each container

$$\Omega = \frac{9!}{2!3!4!} = 1260$$ ways of partitioning 9 letters into 3 containers

IN General, the number of distinct arrangements of N particles into n groups containing $n_1, n_2, \ldots, n_n$ objects is

$$\Omega = \frac{N!}{n_1! n_2! \cdots n_n!} = \frac{N!}{\prod_i n_i!}$$

There is one additional complication.

Each container is a state that each particle can be put into

g_i degenerate states into which n_i particles can be arranged.

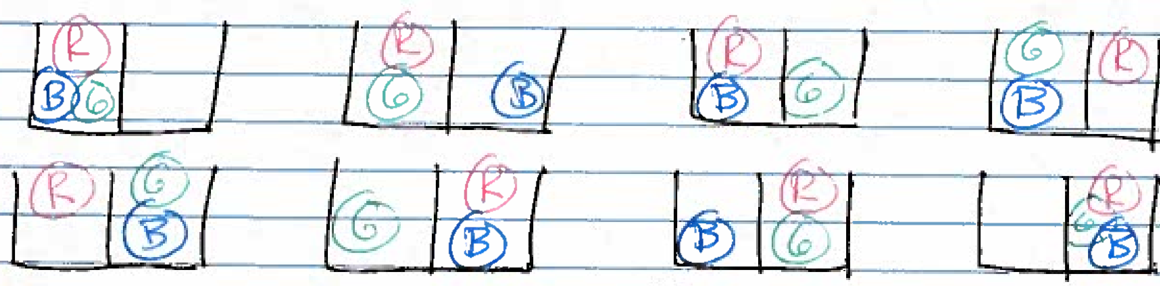
n independent energy levels

Think of this as a system of n containers with g_i subcontainers

Classical case: particles in subcontainers are distinguishable.

EXAMPLE: Consider 2 subcontainers w/ 3 particles

How many arrangements of n_i particles in g_i subcontainers are possible?



8 arrangements or $2^3 \Rightarrow g_i^{n_i}$

The total number of arrangements is then

$$\Omega \equiv \frac{N!}{\prod_i n_i!} \prod_i g_i^{n_i}$$

The most likely macrostate MAXIMIZES Ω while holding N, E CONSTANT.

$$\Rightarrow \quad d\Omega = 0$$

$$d(\ln\Omega) = \frac{1}{\Omega}\, d\Omega = 0 \quad \Rightarrow$$ we can also maximize $\ln\Omega$

$$\ln\Omega = \ln N! + \sum_i n_i \ln g_i - \sum_i \ln n_i!$$

For large N, use Sterling's Formula (Approximation)

$$\ln N! = N\ln N - N$$

$$\ln\Omega \simeq N\ln N \cancel{- N} + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i \cancel{+ \sum_i n_i}^{N}$$

$$\simeq N\ln N + \sum_i n_i \ln\left(\frac{g_i}{n_i}\right)$$

$$d(\ln\Omega) = \underset{N = \text{CONST}}{0} + \sum_i dn_i \ln\left(\frac{g_i}{n_i}\right) + \cancel{n_i} \cdot \frac{n_i}{g_i} \cdot \frac{-g_i}{\cancel{n_i}^2}\, dn_i$$

$$= \sum_i dn_i \ln\left(\frac{g_i}{n_i}\right) - \cancel{\sum_i dn_i}^{\,0} \Leftarrow \text{because } N = \text{CONST}$$

$$= 0$$ to maximize $d(\ln\Omega)$

Now energy conservation $\Rightarrow \sum_i \varepsilon_i\, dn_i = 0$

So we use the method of Lagrange Multipliers to add the Constraints of $dN = dE = 0$

$$\alpha \sum_i dn_i = 0$$

$$-\beta \sum_i \varepsilon_i\, dn_i = 0$$

$$\Rightarrow \quad \sum_i \left[\ln\left(\frac{g_i}{n_i}\right) + \alpha - \beta\varepsilon_i\right] dn_i = 0$$

The only way this is true is if

$$\ln\left(\frac{g_i}{n_i}\right) + \alpha - \beta \varepsilon_i = 0$$

$$\Rightarrow \quad n_i = g_i e^{\alpha} e^{-\beta \varepsilon_i}$$

Now $N = \sum_i n_i = \sum_i g_i e^{\alpha} e^{-\beta \varepsilon_i}$

But e^{α} is a CONST, so can take out of $\sum_i$

$$\Rightarrow \quad e^{\alpha} = \frac{N}{\sum_i g_i e^{-\beta \varepsilon_i}} = \frac{N}{Q} \leftarrow \text{partition function}$$

$$\Rightarrow \quad n_i = g_i \frac{N}{Q} e^{-\beta \varepsilon_i}$$

* Note β has to have units of erg^{-1}!

Boltzmann proved that $\beta = \frac{1}{kT}$ when $k \approx 1.381 \times 10^{-16}$ erg$\cdot$K^{-1} is Boltzmann's CONSTANT.

$$\frac{n_i}{N} = \frac{g_i}{Q} e^{-E_i/kT} \leftarrow$$

IN General $T = T_{ex}$ = excitation temperature

OR

$$\frac{n_i}{n_j} = \frac{g_i}{g_j} e^{-(E_i - E_j)/kT}$$

When all levels are "thermalized"

$T_{ex} = T_K$ gas kinetic temperature of the particles