Quantum Statistical Mechanics

The fundamental assumption of quantum statistical mechanics (QSM) is that in thermal equilibrium every distinct state with the same total energy E, is equally probable.

Consider the N particles with the same mass in an arbitrary potential with one particle energies E_i, $i = 1, 2, \ldots \infty$. The degeneracy for energy E_i is d_i. Let N_i particles be in a state with energy E_i.

$$\therefore \quad \sum_{i=1}^{\infty} N_i = N \quad \text{and} \quad \sum_{i=1}^{\infty} N_i E_i = E.$$

Question :→ How many distinct states correspond to this configuration $\boxed{\text{OR}}$ How many total number of ways $Q[\{N_i\}, i = 1, 2, \ldots]$ can we achieve this.

Answer :→

Case (1) Distinguishable particles.

The particles being distinguishable we need the combination

$${}^{A}C_{B} \equiv \binom{A}{B} \equiv \frac{A!}{[B!][(A-B)!]}, \quad A \geq B,$$

Consider the filling of states with energy E_1 with N_1 particles

$\Rightarrow A = N, \quad B = N_1 \Rightarrow {}^{A}C_{B} = \dfrac{N!}{[N_1!][(N-N_1)!]}$

Now having filled these d_1 states with N_1 particles we can fill them in these states in

$d_1^{N_1}$ ways. Then the total # of ways to fill d_1 states of energy E_1 is

${}^{N}C_{N_1}\, d_1^{N_1}$. After this we have $(N-N_1)$ particles left. We want N_2 of these in d_2 states of energy E_2. # of ways to do this is ${}^{N-N_1}C_{N_2}\, d_2^{N_2}$. For E_3 we get

${}^{N-N_1-N_2}C_{N_3}\, d_3^{N_3}$. For E_i we get

${}^{N-\sum_{j=1}^{i-1} N_j}C_{N_i}\, d_i^{N_i}$. So total # of ways is

$$Q_d(\{N_i\}) = d_1^{N_1} d_2^{N_2} \cdots d_i^{N_i} \cdots \left[\frac{N!}{N_1!\,(N-N_1)!} \times \frac{(N-N_1)!}{N_2!\,(N-N_1-N_2)!} \times \cdots\right]$$

$$\Rightarrow \varphi_d = (N!) \prod_{i=1}^{\infty} \frac{d_i^{N_i}}{[N_i!]}$$, subscript $d \equiv$ distinguishable.

Case (2): Fermions and Bosons, i.e. identical particles

For fermions & bosons it does not make sense to choose N_1 particles out of N to occupy d_1 states of energy E_1 because they are identical. So we only have to calculate the # of ways in which N_i particles occupy d_i states and then multiply these answers $\forall i = 1, 2, \ldots \infty$.

Case (2a): Fermions

Due to antisymmetrization of each state only 1 fermion can occupy one state

$\Rightarrow$ $N_i \leq d_i$. So we have to choose N_i of the d_i states to be occupied. This can be done in

${}^{d_i}C_{N_i}$ ways.

$$\Rightarrow \varphi_F(\{N_i\}) = \prod_{i=1}^{\infty} \frac{d_i!}{[N_i!]\,[(d_i - N_i)!]}$$

Case (2b) Bosons

For bosons we do have the symmetrization constraint on each state. However this does not restrict N_i in any way.

$\Rightarrow 1 \leq N_i \leq N$ just as for distinguishable particles. So now we use a trick of denoting particles by circles and different states by crosses. Let there be N_i ~~sta~~ particles $\Rightarrow N_i$ circles. To make d_i partititions of a finite box we need $d_i - 1$ dividing crosses. So we have a total of $N_i + d_i - 1$ objects of which we want to choose N_i objects. ~~as~~ So we get

$$^{N_i+d_i-1}C_{N_i} \equiv \frac{(N_i+d_i-1)!}{[N_i!][(d_i-1)!]}$$ ways of achieving this goal. Then we get

$$\varphi_B(\{N_i\}) = \prod_{i=1}^{\infty} \frac{(N_i+d_i-1)!}{[N_i!][(d_i-1)!]}$$

The most probable configuration in thermal equilibrium is one in which $\varphi(\{N_i\})$ is a maximum. We need to find this maximum. We have two constraints i.e. the total # of particles is fixed

$$\Rightarrow \sum_{i=1}^{\infty} N_i = N, \longrightarrow (5.78)$$

and the total energy is fixed

$$\sum_{i=1}^{\infty} N_i E_i = E \longrightarrow (5.79)$$