Elements of Statistical Mechanics

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Abstract

Concept of phase-space, derivation of S=klogW, types of ensembles-Maxwell-Boltzmann statistics, Bose-Einstein statistics, Fermi-Dirac statistics-photon gas-Planck's law of black body radiation distribution-Rayleigh Jeans and Wi en's law.

1 Introduction

The microscopic properties of individual particles are parameters like size, mass, velocities. Macroscopic properties are parameters like temperature, pressure, etc. When we study a system with a large number of particles, it is not possible and also not required, to write equations of motion of each particle. We study such systems using statistics of microscopic properties and relate them to the macroscopic properties of the system. For example, the temperature and pressure of a gas depend on the motion of gas molecules. Many microscopic states can lead to the same macroscopic state. If the macroscopic parameters of an isolated system do not change with time, then the system is said to be in equilibrium.

Phase space is a space in which all possible states of system are represented. Each free particle in phase space has three position variables and three momentum variables (6 dimensional space, x, y, z, p_x, p_y, p_z). If the system consists of N particles then a point in the 6N dimensional space describes the state of every particle in that system. By uncertainty principle, $\Delta x \Delta p_x \geq h$, and therefore at a given time a particle occupies a cell of size h.

A collection of large number of microscopically identical particles is called an ensemble. A Micro canonical ensemble is a collection of large number of essentially independent systems having same energy E, same volume V and same number of particles N. A Canonical ensemble is a collection of large number of essentially independent systems having same temperature T, same volume V and same number of particles N. A Grand canonical ensemble is a collection of large number of essentially independent systems having temperature T, same volume V and the chemical potential μ.

2 Probability theorem

Consider a large box divided into k cells whose areas are a1,a2,a3.. We throw N balls onto the box in a completely random manner so that no part of box is favored. After a great number of repetitions we find that a certain distribution occurs more often than any other known as most probable distribution. Most probable distribution may or may not be found after a particular throw but is more likely to be found later. The probability of a certain distribution is given by

$$W = GM$$

G is prior, based on the properties of the cell (for example, the area of the cell) M is thermodynamic probability in which balls are distributed.

The number of ways in which N distinguishable particles can be used to select n_1 no of particles is

$$\frac{N!}{(N-n_1)!(n_1)!}$$

The number of ways n_2 particles can be selected from the remaining $N - n_1$ particles is

$$\frac{(N-n_1)!}{(N-n_1-n_2)!(n_2)!}$$

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Repeating this process over k states, we get

$$\frac{N!}{(N-n_1)!(n_1)!} \times \frac{(N-n_1)!}{(N-n_1-n_2)!(n_2)!} \times \frac{(N-n_1-n_2)!}{(N-n_1-n_2-n_3)!(n_3)!} = \frac{N!}{n_1!n_2!n_3!....n_k!}$$

The probability g_i of a ball to fall in a cell to area a_i n number of times is

$$g_i = a_i^n$$

If all the cells are of equal area, then the probability of n_i balls in cells of area a_i

$$G = a_1^{n_1} a_2^{n_2} a_3^{n_3} ....$$

$$G = a^{n_1+n_2+n_3.......+n_k} = a^N$$

3 Boltzmanns theorem on entropy and probability

According to Boltzmann, the equilibrium state of the system is the state of maximum probability. From the thermodynamic point of view, the equilibrium state of the system is the state of maximum entropy. Thus in equilibrium both the entropy and thermodynamic probability have their maximum values. Hence, Boltzmann concluded that entropy is a function of probability. i.e., S = f(W) Consider a system made up of two systems which has a total entropy S and W is the maximum probability of the combined system in a definite state. Each of the systems has entropy S_1 and S_2 and maximum probabilities W_1 and W_2.

Then their entropies are given by S_1 = f(W1) and S_2 = f(W2)

Total entropy of two systems is $S_1 + S_2 = f(W_1) + f(W_2)$

The combined probability can be written as $f(W_1) + f(W_2) = f(W_1, W_2)$

Therefore $S_1 + S_2 = f(W_1, W_2)$

Differentiating wrt W_1

$$W_2 f'(W_1, W_2) = f'(W_1)$$

Differentiating wrt W_2

$$W_1 f'(W_1, W_2) = f'(W_2)$$

Dividing the above two equations

$$\frac{W_2}{W_1} = \frac{f'(W_1)}{f'(W_2)} = k$$

Similarly,

$$W_1 f'(W_1) = W_2 f'(W_2) = W_3 f'(W_3) = ... = k$$

Integrating

$$\int f'(W_1) = \int \frac{k}{f(W_1)}, \int f'(W_2) = \int \frac{k}{f(W_2)}$$

$$f(W_1) = klnW_1 + c_1$$

$$f(W_2) = klnW_2 + c_2$$

Applying boundary condition W=1, S=0, c=0

Therefore

$$f(W) = klnW$$

4 Maxwell– Boltzmann Statistics

This applies to systems where: 1. The particles are identical, distinguishable 2. The total number of particles in the system is always constant.

$$\Sigma n_i = n_0 + n_1 + n_2 + n_3 + ----- = N = constant$$

3. The sum of energies of all the particles is constant.

$$\Sigma n_i E_i = n_1 E_1 + n_2 E_2 + n_3 E_3 + --------- = E = constant$$

4. Each quantum state can have 0,1,2,3....n particles

The number of ways in which N distinguishable particles can be used to select n_1 no of particles is

$$\frac{N!}{(N-n_1)!(n_1)!}$$

The number of ways n_2 particles can be selected from the remaining $N-n_1$ particles is

$$\frac{(N-n_1)!}{(N-n_1-n_2)!(n_2)!}$$

Repeating this process over k states, we get

$$\frac{N!}{(N-n_1)!(n_1)!} \times \frac{(N-n_1)!}{(N-n_1-n_2)!(n_2)!} \times \frac{(N-n_1-n_2)!}{(N-n_1-n_2-n_3)!(n_3)!} = \frac{N!}{n_1!n_2!n_3!....n_k!}$$

If g_i is the probability of locating a particle in a certain state E, then the total probability of n_i particles in state g_i is

$$G = g_1^{n_1} g_2^{n_2}......g_k^{n_k}$$

The total probabaility is

$$P = \frac{N!}{n_1!n_2!n_3!....n_k!} \times g_1^{n_1} g_2^{n_2}......g_k^{n_k}$$

$$P = N!\Pi\frac{g_i^{n_i}}{n_i!}$$

Taking ln on both sides

$$lnP = lnN! + \Sigma(lng_i^{n_i} - lnn!)$$

Applying Stirling's formula

$$lnn! = nlnn - n$$

$$lnP = NlnN - N + \Sigma[n_i lng_i - (n_i lnn_i - n_i)$$

In statistial equilibrium, we have the most probabale distribution P$_{max}$ is when $\delta P_{max} = 0$

$$\delta(lnP_{max}) = \Sigma(\delta n_i ln(g_i/n_i) = 0$$

We know,

$$\Sigma\delta n_i = 0, \Sigma(\delta n_i E_i) = 0$$

Using the method of Lagrange's undetermined multipliers α, β

$$\Sigma(\alpha\delta n_i) = 0, \Sigma(\beta\delta n_i E_i) = 0$$

$$\Sigma(\delta n_i ln(g_i/n_i) = 0$$

$$\delta(lnP_{max}) = 0 = \Sigma(\delta n_i ln(g_i/n_i) - (\Sigma(\alpha\delta n_i) + \Sigma(\beta\delta n_i E_i))$$

$$\delta n_i(ln(g_i/n_i)) = \Sigma\delta n_i(\alpha + \beta E_i)$$

As the variation in δn_i is independant of each other we can cancel off the $\Sigma\delta n_i$

$$ln(g_i/n_i) = \alpha + \beta E_i$$

$$e^{-(\alpha+\beta E_i)} = \frac{n_i}{g_i}$$

$$n_i = \frac{g_i}{e^{(\alpha+\beta E_i)}}$$

The above equation represents Maxwell-Boltzmann distribution.

5 Bose–Einstein Statistics

This applies to systems where: 1. The particles are identical, indistinguishable 2. The total number of particles in the system is always constant.

$$\Sigma n_i = n_0 + n_1 + n_2 + n_3 + - - - - - = N = constant$$

3. The sum of energies of all the particles is constant.

$$\Sigma n_i E_i = n_1 E_1 + n_2 E_2 + n_3 E_3 + - - - - - - - - - = E = constant$$

4. The particles have an integral spin=0,1,2,3...and do not satisfy Pauli Exclusion Principle, ie, each quantum state can have 0,1,2,3....n particles Eg: Bosons, Photons, Mesons etc.

The number of ways in which N indistinguishable particles can be used to select n_1 no of particles in g_i states is

$$\frac{(n_i + g_i - 1)!}{(g_i - 1)!(n_1)!}$$

where $g_i - 1$ is the number of partitions As the number of particles n_i and the number of possible states is very large, we can assume

$$(n_i + g_i - 1)! \approx (n_i + g_i)!$$

The total probabaility is

$$P = \Pi \frac{(n_i + g_i)!}{(g_i - 1)!(n_i)!}$$

Taking ln on both sides

$$lnP = \Sigma(ln(n_i + g_i)! - ln(g_i - 1)! - ln(n_i)!)$$

Applying Stirling's formula

$$lnn! = nlnn - n$$

$$lnP = \Sigma((n_i + g_i)ln(n_i + g_i) - (n_i + g_i) - (g_i - 1)ln(g_i - 1) + (g_i - 1) - (n_i)ln(n_i) + n_i$$

$$lnP = \Sigma((n_i + g_i)ln(n_i + g_i) - ((g_i - 1)ln(g_i - 1) - 1) - (n_i)ln(n_i)))$$

In statistical equilibrium, we have the most probabale distribution P$_{max}$ is when $\delta P_{max} = 0$,$\delta g_i = 0$

$$\delta lnP_{max} = \Sigma(\delta n_i(ln(g_i + n_i) - ln(n_i))) = 0$$

We know,

$$\Sigma \delta n_i = 0, \Sigma(\delta n_i E_i) = 0$$

Using the method of Lagrange's undetermined multipliers α, β

$$\Sigma(\alpha \delta n_i) = 0, \Sigma(\beta \delta n_i E_i) = 0$$

$$\delta(lnP_{max}) = 0 = \Sigma(\delta n_i ln(\frac{g_i + n_i}{n_i}) - (\Sigma(\alpha \delta n_i) + \Sigma(\beta \delta n_i E_i))$$

$$\delta n_i(ln(\frac{g_i + n_i}{n_i}) = \Sigma \delta n_i(\alpha + \beta E_i)$$

As the variation in δn_i is independant of each other we can cancel off the $\Sigma \delta n_i$

$$ln\frac{n_i}{(g_i + n_i)} = -(\alpha + \beta E_i)$$

$$e^{-(\alpha + \beta E_i)} = \frac{n_i}{g_i + n_i}$$

$$n_i = \frac{g_i}{e^{(\alpha + \beta E_i)} - 1}$$

The above equation represents Bose-Einstein distribution.

6 Fermi–Dirac Statistics

1. The particles are identical, indistinguishable 2. The total number of particles in the system is always constant.

$$\Sigma n_i = n_0 + n_1 + n_2 + n_3 + - - - -- = N = constant$$

3. The sum of energies of all the particles is constant.

$$\Sigma n_i E_i = n_1 E_1 + n_2 E_2 + n_3 E_3 + - - - - - - - - = E = constant$$

4. The particles have half integral spin=0,1/2,3/2,...and satisfy Pauli Exclusion Principle, ie, each quantum state can have only 1 particle, Eg: electrons, etc.

The number of ways in which g_i states can be occupied is

$$P = \frac{g_i!}{(g_i - n_i)!(n_i)!}$$

The total probabaility is

$$P = \Pi \frac{g_i!}{(g_i - n_i)!(n_i)!}$$

Taking ln on both sides

$$lnP = \Sigma(lng_i! - ln(g_i - n_i)! - ln(n_i)!)$$

Applying Stirling's formula

$$lnn! = nlnn - n$$

$$lnP = \Sigma(g_i lng_i - g_i - ((g_i - n_i)ln(g_i - n_i) + (g_i - n_i) - n_i lnn_i + n_i)$$

$$lnP = \Sigma(g_i lng_i - ((g_i - n_i)ln(g_i - n_i) - n_i ln(n_i))$$

In statistial equilibrium, we have the most probable distribution P$_{max}$ is when $\delta P_{max} = 0$,$\delta g_i = 0$

$$\delta lnP_{max} == 0 = \Sigma(-\delta n_i(ln(g_i - n_i)) - ln(n_i))$$

$$= \Sigma(-\delta n_i(ln(\frac{g_i - n_i}{n_i})$$

We know,

$$\Sigma \delta n_i = 0, \Sigma(\delta n_i E_i) = 0$$

Using the method of Lagrange's undetermined multipliers α, β

$$\Sigma(\alpha \delta n_i) = 0, \Sigma(\beta \delta n_i E_i) = 0$$

$$\Sigma(-\delta n_i(ln(\frac{g_i - n_i}{n_i}) + (\Sigma(\alpha \delta n_i) + \Sigma(\beta \delta n_i E_i)) = 0$$

$$\Sigma(-\delta n_i(ln(\frac{g_i - n_i}{n_i}) + (\alpha + \beta E_i)) = 0$$

As the variation in δn_i is independant of each other we can cancel off the $\Sigma \delta n_i$

$$ln\frac{(g_i - n_i)}{n_i} = (\alpha + \beta E_i)$$

$$e^{(\alpha + \beta E_i)} = \frac{(g_i - n_i)}{n_i}$$

$$n_i = \frac{g_i}{e^{(\alpha + \beta E_i)} + 1}$$

The above equation represents Fermi-Dirac distribution.

Table 1: Comparison of statistical distributions

	Max-Boltz	Bose-Einstein	Fermi-Dirac
Identical Particles	yes	yes	yes
Distinguishable Particles	yes	no	no
Spin	no	integral(0,1,2,3..)	half-integral(1/2,3/2,..)
Pauli-Exclusion Principle	no	no	yes
Probability	$P = \frac{{g_i}^{n_i} N!}{n_i}$	$P = \frac{(n_i+g_i-1)!}{(g_i-1)!(n_i)!}$	$P = \frac{g_i!}{(g_i-n_i)!(n_i)!}$
Distribution	$n_i = \frac{g_i}{e^{(\alpha+\beta E_i)}}$	$n_i = \frac{g_i}{e^{(\alpha+\beta E_i)}+1}$	$n_i = \frac{g_i}{e^{(\alpha+\beta E_i)}-1}$