The critical observation

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The Critical Observation of Possibility Analysis of Particles in the Maxwell - Boltzmann Distribution Law

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Abstract

J. C. Maxwell developed his kinetic theory of gases in 1859. Maxwell determined the distribution of velocities among the molecules of a gas. His finding was later generalized in 1871 by Ludwig Boltzmann to express the distribution of energy levels among the molecules. This paper describes the critical observation of probability comparison of particles displacement in each energy level and mean energy from each particles. The initial conditions is the system consists of 4000 particles where 2000 particles at the first energy level, 1700 particles at the second energy level, 300 particles at the third energy level. Each energy level has the same intrinsic probability. The energy at the first level (ε_1), second (ε_2) and thirds (ε_3) levels are 0 eV, 1 eV, and 2eV, respectively. The probability comparison when three particles which initially occupied the second energy level where two of the particles being excited to the first energy level and the single one fell to the third energy level is 50% from the initial probability distribution.

Keywords: Probability distribution, Maxwell-Boltzmann distribution, particles displacement

1 Introduction

The statistical mechanics is a widely known method that is used to acquire mutual complexion along particle or macroscopic properties of a physical system. This method is a tool for studying the particle properties in large numbers based on the dynamic behavior of macroscopic basis. In order to perform a statistical analysis of a particle system, we have to do a proper calculation of the dynamical state of each particle based on the general characteristic of particles. This calculation introduce the concept of particle distribution probability between different dynamical circumstances of the particles.

2 Statistical Equilibrium

A closed, classical and isolated system with N-particles is proportional with the particle volume (V),

$$\begin{aligned} &N \propto V \\ &N \approx 10^{23} \text{ Molecules, } V \approx 10^{23} \text{ Volume from molecules} \end{aligned} \tag{1}$$

Therefore, using thermodynamic limit namely partition system, it can be approximate that:

$$N \to \infty \text{ and } V \to \infty \tag{2}$$

so that the n-particle density ($n = N/V$) has a finite value. If the particles of the system has no interaction with each other, and every state of energy level ($\varepsilon_1, \varepsilon_2, \varepsilon_3, ...$) will have $n_1, n_2, n_3, ...$ particles consecutively. The number of particles and total energy of the system are [1],

$$N = \sum_i n_i \text{ and } E = \sum_i n_i \varepsilon_i \tag{3}$$

Total energy system in equation (3) is obtained by assuming that the particles do not interact with each other. It will change the particle distribution in each state of energy. $n_1, n_2, n_3, ...$ shows the particle distribution among the N particles that exist in the state of energy. If the distribution probabilities have been achieved, it is said that the system is in a statistical equilibrium condition [2].

3 Maxwell-Boltzmann Distribution Law

The geometric picture of the $n_1, n_2, n_3, ..$ distribution is shown in Fig 1. Each horizontal line represents a particular energy states (ε_i) and the number of points shows the number of particles in each energy state (n_i). In Fig 1, $n_1 = 3, n_2 = 2, n_3 = 0, n_4 = 1, n_5 = 4$, and $n_6 = 2$.

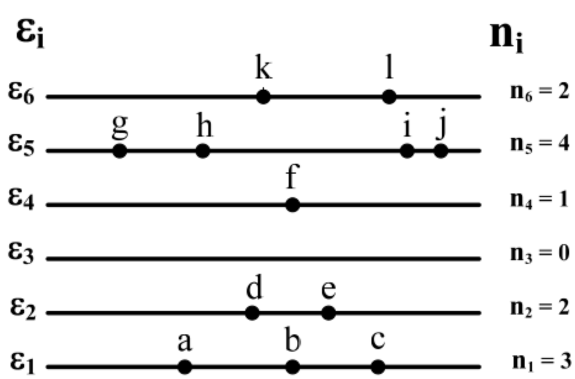

Fig 1. Particle distribution a different energy level.

There are N ways to choose the first particle in a system. For the selection of the second particle will have $(N-1)$ different ways. In the third particle are $(N-2)$ in different ways. The total number of ways to choose the first three particles to be placed at the energy level ε_1 is [1] [2] [4]:

$$N(N-1)(N-2) = \frac{N(N-1)(N-2)(N-3)!}{(N-3)!} = \frac{N!}{(N-3)!} \tag{4}$$

If the three particles were labeled a, b, and c, then it can be arranged in 3! = 6 ways which are abc, bac, cab, acb, bca, cba. 3! is a permutation of the particles a, b and c in the ε_1 energy level. To obtain the total number of ways to choose the first three particles from any energy level, then the equation (4) is divided by 3!.

$$N(N-1)(N-2)=\frac{N!}{(N-3)!\ 3!} \tag{5}$$

To obtain the total number of ways to place the n_1 particles at energy level (ε_1) is,

$$\frac{N!}{(N-n_1)!\ n_1!} \tag{6}$$

In the second condition (ε_2) are $(N-n_1)$ particles. To get the total number of ways is to place n_2 particles at the ε_2 energy level. We can use equation (6) by replacing N with $(N-n_1)$ and n_1 with n_2,

$$\frac{(N-n_1)!}{(N-n_1-n_2)!\ n_2!} \tag{7}$$

Subsequently to place n_3 particles at energy level ε_3,

$$\frac{(N-n_1-n_2)!}{(N-n_1-n_2-n_3)!\ n_3!} \tag{8}$$

Total number of ways to obtain the $n_1, n_2, n_3, \ldots$ particles distribution from equation (6) to (8) to give probability, P [1-4],

$$P=\frac{N!}{(N-n_1)!\ n_1!}\cdot\frac{(N-n_1)!}{(N-n_1-n_2)!\ n_2!}\cdot\frac{(N-n_1-n_2)!}{(N-n_1-n_2-n_3)!\ n_3!}\cdots$$
$$P=\frac{N!}{n_1!\ n_2!\ n_3!} \tag{9}$$

Furthermore, the particle distribution probability based on Fig 1 is,

$$P=\frac{N!}{3!\ 2!\ 0!\ 1!\ 4!\ 2!} \tag{10}$$

All the energy levels have the same occupancies probability. However it is possible for a state to have different intrinsic probability. For example, a particular condition can be attributed to the round momentum state that is different than the other state. If used in the calculation of intrinsic probability, P will change its shape. If g_i is the probability of finding a particle at energy level ε_i, then the probability of finding two particles at the energy level are $g_i \cdot g_i = g_i^{\,2}$. For n_i particles, the probability to find n_i particles at energy level ε_i is $g_i^{\,n_i}$, so the total probability of the limiting energy levels are [3]:

$$P=\frac{N!g_1^{\,n_1}\cdot g_2^{\,n_2}\cdot g_3^{\,n_3}\cdots}{n_1!n_2!n_3!\cdots} \tag{11}$$

If all particles are identical and indistinguishable from each other or we are not able to know the difference between them, then N! is a particle permutation of occupying the state of different energy levels and will provide the same energy barrier. This means that the distribution probability in equation (9) must be divided by N!, in order to obtain the statistical distribution of Maxwell –

Boltzmann equation [3],

$$P = \frac{g_1^{\,n_1} \cdot g_2^{\,n_2} \cdot g_3^{\,n_3} \cdots}{n_1! n_2! n_3! \cdots} = \prod_{i=1}^{N} \frac{g_i^{\,n_i}}{n_i\,!} \tag{12}$$

4 Partition Equilibrium

The barrier energy level will explain the restriction that has the greatest probability or equilibrium partition, i.e. $dP = 0$. In mathematics, it is easy to obtain the maximum value of $\ln P$. Because $d(\ln P) = P^{-1} dP = 0$ for $dP = 0$. From equation (12), will be obtained,

$$\begin{aligned} \ln P &= n_1 \ln g_1 + n_2 \ln g_2 + n_3 \ln g_3 + \ldots. \\ &\quad - \ln n_1! - \ln n_2! - \ln n_3! + \ldots. \end{aligned} \tag{13}$$

By using *stirling* equation

$$\ln x! = x \ln x - x \tag{14}$$

from equation (13),

$$\begin{aligned} \ln P &= n_1 \ln g_1 + n_2 \ln g_2 + n_3 \ln g_3 + \ldots.. \\ &\quad - (n_1 \ln n_1 - n_1) - (n_2 \ln n_2 - n_2) - (n_3 \ln n_3 - n_3) - \ldots.. \end{aligned} \tag{15}$$

$$\ln P = -n_1 \ln \frac{n_1}{g_1} - n_2 \ln \frac{n_2}{g_2} - \ldots.. + (n_1 + n_2 + \ldots..)$$

Considering $N = \sum_i n_i$ using summing sign (Σ), equation (15) can be written

$$\ln P = N - \sum_i n_i \ln \frac{n_i}{g_i} \tag{16}$$

If N = constant, then

$$dN = \sum_i dn_i = 0 \tag{17}$$

$$\begin{aligned} d(\ln P) = dN &= -\sum_i (dn_i) \ln \frac{n_i}{g_i} - \sum_i n_i d\left(\ln \frac{n_i}{g_i} \right) \\ &= -\sum_i (dn_i) \ln \frac{n_i}{g_i} - \sum_i n_i \frac{g_i}{n_i} \frac{dn_i}{g_i} \\ &= -\sum_i (dn_i) \ln \frac{n_i}{g_i} - \sum_i dn_i \end{aligned} \tag{18}$$

by applying equation (17), (18) and $d(\ln P) = 0$,

$$d(\ln P) = -\sum_i (dn_i) \ln \frac{n_i}{g_i} = 0 \tag{19}$$

If all changes in $dn_1, dn_2, dn_3, \ldots$ values is arbitrary, then equation (19) will be met if,

$$\ln\frac{n_1}{g_1} = \ln\frac{n_2}{g_2} = \ln\frac{n_3}{g_3} = ... = 0 \text{ or } \ln\frac{n_1}{g_1} = \ln\frac{n_2}{g_2} = \ln\frac{n_3}{g_3} = ... = \ln 1 \quad (20)$$

$$n_1 = g_1;\ n_2 = g_2;\ n_3 = g_3;\ldots\ldots \quad (21)$$

requirements of equation (17) is $\sum_i dn_i = 0$, then dn_i is in fact not an arbitrary value. Internal energy of the system is constant (E = constant), then from equation (3),

$$dE = \sum_i \varepsilon_i\, dn_i = 0 \quad (22)$$

Compensation of the two conditions of equation (17) and (22), α and β parameters commonly known as the unknown multiplier. By doubling the equation (17) and (22) then summing them into equation (19), it will obtain,

$$\sum_i\left(\ln\frac{n_i}{g_i}\right)dn_i + \alpha\sum_i dn_i + \beta\sum_i \varepsilon_i dn_i = \sum_i\left(\ln\frac{n_i}{g_i} + \alpha + \beta\varepsilon_i\right)dn_i = 0 \quad (23)$$

Two coefficients α and β are used only for the compensation of two restriction equation (17) and (22). Equilibrium distribution can be obtained, if:

$$\ln\frac{n_i}{g_i} + \alpha + \beta\varepsilon_i = 0 \quad (24)$$

or

$$n_i = g_i\, e^{-\alpha-\beta\varepsilon_i} \quad (25)$$

Equation (25) is the partition with the maximum probability. While the two parameters α and β are a interconnected with the physical properties of the system.

$$N = \sum_i n_i = \sum_i g_i e^{-\alpha} e^{-\beta\varepsilon_i} = e^{-\alpha}\sum_i g_i\, e^{-\beta\varepsilon_i} = e^{-\alpha} Z \quad (26)$$

where,

$$Z = \sum_i g_i\, e^{-\beta\varepsilon_i} \quad (27)$$

Z is the limiting function. This expression is important and frequently encountered in many calculations. From equation (25) and (26), we can obtain,

$$e^{-\alpha} = \frac{N}{Z} = \frac{n_i}{g_i} e^{\beta\varepsilon_i} \text{ or } e^{-\alpha} = \frac{N}{Z} g_i\, e^{\beta\varepsilon_i} \quad (28)$$

which is well known the Maxwell – Boltzman distribution law.

5 Sample Case

Initial condition of a system consist of 4000 particles which occupy energy levels, $\varepsilon_1 = 0$, $\varepsilon_2 = \varepsilon$ and $\varepsilon_3 = 2\varepsilon$ where each energy level has the same intrinsic probability. The initial conditions are 2000, 1700, 300 particles in ε_1, ε_2 and ε_3

respectively. The highest occupancy probability is according to Fig 1.

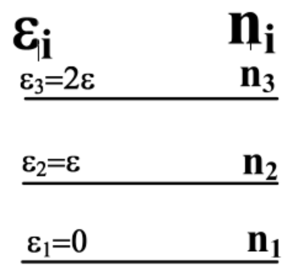

Fig 2. Initial condition of a system.

Initial condition : $N=\sum_i n_i = n_1+n_2+n_3 = 4000$

Total energy can be determined by,

$$E=\sum_i n_i\varepsilon_i = n_1\ \varepsilon_1 + n_2\ \varepsilon_2 + n_3\ \varepsilon_3$$

$$=2000(0)+1700(\varepsilon)+300(2\varepsilon)=2300\ \varepsilon$$

Energy barrier with a maximum probability is,

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

Considering $g_1=g_2=g_3=g$,

$$n_1 = g_1 e^{-\alpha-\beta\varepsilon_1} = ge^{-\alpha}$$

$$n_2 = g_2 e^{-\alpha-\beta\varepsilon_2} = ge^{-\alpha-\beta\varepsilon}$$

$$n_3 = ge^{-\alpha-\beta\varepsilon_3} = ge^{-\alpha-2\beta\varepsilon}$$

If given the assumptions for $e^{-\beta\varepsilon}$, then:

$$n_1 = ge^{-\alpha} \text{ and } n_2 = ge^{-\alpha}\cdot e^{-\beta\varepsilon} = n_1 x \text{ and } n_3 = ge^{-\alpha}\cdot e^{-2\beta\varepsilon} = n_1 x^2$$

Then,

$$n_1+n_2+n_3=4000$$

$$n_1+n_1x+n_1x^2=4000 \text{ or } n_1(1+x+x^2)=4000 \qquad (29)$$

$$\sum_i n_i\varepsilon_i = 2300$$

$$n_1\varepsilon_1+n_2\varepsilon_2+n_3\varepsilon_3 = 2300\varepsilon \text{ or } n_1(0)+n_1x(\varepsilon)+n_1x^2(2\varepsilon)=2300\varepsilon$$

$$n_1\left(x+2x^2\right)=2300 \qquad (30)$$

by swapping n_1 from equation (29) and (30)

$$\frac{\left(1+x+2x^2\right)}{\left(x+2x^2\right)}=\frac{4000}{2300}$$

$$23\left(1+x+2x^2\right)=40\left(x+2x^2\right), \text{ then } 57x^2+17x-23=0$$

$$x=\frac{-17\pm\sqrt{(17)^2-4(57)(-23)}}{2(57)}=\frac{-17\pm 74.38}{114}\ x_1=0.5033 \quad \text{and} \quad x_2=-0.8016$$

by substituting $x_1 = 0.5033$ into equation (29),

$$n_1(1+0.5033+(0.5033)^2)=4000$$

$$n_1(1.7568)=4000, \text{therefore } n_1=2276.9=2277$$

$$n_2=n_1x=2277(0.5033)=1146, \quad n_3=n_1x^2=2277(0.5033)^2=577$$

Maxwell – Boltzmann distribution probability [4],

$$P=\prod_{i=1}^{N}\frac{g_i^{\ n_i}}{n_i}=\frac{g_1^{\ n_1}\cdot g_2^{\ n_2}\cdot g_3^{\ n_3}}{n_1!n_2!n_3!}=\frac{g^{n_1+n_2+n_3}}{n_1!n_2!n_3!}$$

$$=\frac{g^{2277+1146+577}}{2277!\ 1146!\ 577!}=\frac{g^{4000}}{2277!\ 1146!\ 577!}$$

At another conditions, the three particles move from energy level ε_2; two particles to the energy level ε_1 and one particle to the energy level ε_3. After the transition, $n_1=2279$, $n_2=1143$, $n_3=578$. The probability of this condition, is

$$P^{'}=\frac{g_1^{\ n_1}\cdot g_2^{\ n_2}\cdot g_3^{\ n_3}}{n_1!n_2!n_3!}=\frac{g^{2279+1143+578}}{2279!\ 1143!\ 578!}=\frac{g^{4000}}{2279!\ 1143!\ 578!}$$

$$\frac{P^{'}}{P}=\frac{2277!\ 1146!\ 577}{2279!\ 1143!\ 578!}=\frac{1146\times1145\times\ 577}{2278\times2279\times578}=0.5=50\%$$

6 Conclusion

The initial condition consist of particles n_1 = 2000, n_2 = 1700 particles and n_3 = 300. Amount of energy at every level; 0 eV for ε_1, 1eV to ε_2, and 2eV to ε_3. At this energy level, will produce changes in the number of particles is 2277 particles n_1, n_2 = 577 particles and n_3 = 1146 particles. Displacement of the particle energy level ε_2 comprising: 2 particles to ε_1 energies and single particle to ε_3 energy level. The number of particles after the transfer are n_1 = 2279, n_2 = 1143 particles and n_3 = 578 particles. The possibility of probability in this state by 50%.

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