

Change of Entropy and Equilibrium condition

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Abstract:

The Clausius inequality relation of entropy change and Boltzmann expression of entropy are used to derive three statistical distributions, partition function as well as Helmholtz energy, Gibbs energy and chemical potential as equilibrium properties of the system. The chemical potential of all particles of the system are equal irrespective of their occupied energy level. The derivation of statistical distributions avoids the calculus of variation and Lagrange undetermined multipliers which are unavoidable to derive partition function and three statistical distributions using the statistical thermodynamics.

Keywords:

Statistical distributions, partition function, Helmholtz energy, Gibbs energy, chemical potential.

1. Introduction

The Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistical distribution laws, partition function appear to have a little common area of overlapping with the chemical equilibrium, chemical potential, Helmholtz and Gibbs energy. The first group of topics is mostly important to a student of physics while the second group is very important to a student of chemistry. However, all of the topics of first group and second group have a common origin, the law of entropy change. In this discussion, we shall try to find out the role of entropy change in all these topics of diverse field. The entropy itself is not very well understood as a real physical property of a system but mathematically the Boltzmann relation of entropy serves very good purpose of calculating entropy change and this will serve most of our purpose.

2. Entropy Change

The Clausius inequality relation of the change of entropy S is given by

$$\Delta S \geq q/T \quad (1)$$

where q is the heat absorbed by system at temperature T . The ΔS is greater than q/T if process of heat absorption is irreversible and it is equal to ΔS when the process is reversible. The first law of thermodynamics expresses the increase of the internal energy ΔE of the closed system (where the number of particles of the system is constant) as

$$\Delta E = q + w \quad (2)$$

here q is the heat absorbed and w is the work done on the system. The w is the sum of pressure-volume work w_{pv} , and the work other than pressure-volume type work w_{non-pv} , done on the system. In case $\Delta v = 0$ and non-p-v work is negligible, the work ($w=0$) and in a reversible process of heat absorption,

$$\Delta E = q = T \Delta S \quad (3)$$

Let our system contains N indistinguishable and noninteracting particles confined in volume V at temperature T with total energy E such as,

$$N = \sum_r n_r, E = \sum_r n_r \epsilon_r \quad (4)$$

where n_r is the number of particles, each with energy ϵ_r in the r th energy level at equilibrium. If g_r is the number of degeneracies of the r th energy level, the distinct arrangements^{1,2a} Ω for correct Boltzmann Ω (MB), Bose-Einstein Ω (BE) and Fermi-Dirac Ω (FD) counting's are as follows,

$$\Omega \text{ (MB)} = \prod_r g_r^{n_r} / n_r! \quad (5)$$

$$\Omega \text{ (BE)} = \prod_r (n_r + g_r - 1)! / [n_r! (g_r - 1)!] \quad (6)$$

$$\Omega \text{ (FD)} = \prod_r g_r! / [n_r! (g_r - n_r)!] \quad (7)$$

The Boltzmann expression of entropy S_{eq} for each distribution at equilibrium of the system is,

$$S_{eq} = k \ln \Omega \quad (8)$$

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here k is the Boltzmann constant. As we know the equilibrium state of the system is the state where distribution of particles in different energy level remains constant under unchanged macroscopic conditions such as pressure, volume and temperature.

At equilibrium, the expression for entropy of Maxwell-Boltzmann distribution is

$$S_{eq} = k \ln \prod_r g_r^{n_r}/n_r! \tag{9}$$

If a particle is transferred from i th to j th energy level reversibly without performing any work, the change of entropy from S_{eq} to S_{ij} becomes

$$\begin{aligned} \Delta S(MB) &= S_{ij} - S_{eq} = k \ln \prod_{r \neq i,j} g_r^{n_r}/n_r! \cdot [g_i^{n_i-1}/(n_i-1)!] \cdot [g_j^{n_j+1}/(n_j+1)!] - k \ln \prod_r g_r^{n_r}/n_r! \\ &= k \ln (n_i/g_i)(g_j/n_j)[n_j/(n_j+1)] \end{aligned} \tag{10}$$

For the same condition of the transfer of a particle from i th to j th energy level, the entropy change of Bose-Einstein and Fermi-Dirac distributions are,

$$\begin{aligned} \Delta S(BE) &= k \ln \prod_{r \neq i,j} (n_r + g_r - 1)!/[n_r!(g_r - 1)!] \cdot [(n_i - 1) + g_i - 1]/(n_i - 1)!(g_i - 1)! \cdot [(n_j + 1) + g_j - 1]/[(n_j + 1)!(g_j - 1)!] \\ &\quad - k \ln \prod_r (n_r + g_r - 1)!/[n_r!(g_r - 1)!] \\ &= k \ln n_i/(n_i + g_i - 1) \cdot (n_j + g_j)/(n_j + 1) \end{aligned} \tag{11}$$

$$\begin{aligned} \Delta S(FD) &= k \prod_{r \neq i,j} g_r!/[n_r!(g_r - n_r)!] \cdot g_i!/[n_i - 1]! \cdot (g_i - n_i - 1)! \cdot g_j!/[n_j + 1]!(g_j - n_j + 1)! - k \ln \prod_r g_r!/[n_r!(g_r - n_r)!] \\ &= k \ln n_i/(g_i - n_i + 1) \cdot (g_j - n_j)/(n_j + 1) \end{aligned} \tag{12}$$

The ΔS from Clausius relation of entropy change from relation (3) due to transfer of a particle from i th to j th energy level reversibly without performing any work is,

$$\Delta S = (\epsilon_j - \epsilon_i)/T \tag{13}$$

Equating entropy change (13) with relations (10) to (12), and for (10)

$$\begin{aligned} k \ln (n_i/g_i)(g_j/n_j)[n_j/(n_j+1)] &= (\epsilon_j - \epsilon_i)/T \\ k \ln (g_j/n_j) + k \ln [n_j/(n_j+1)] - \epsilon_j/T &= k \ln (g_i/n_i) - \epsilon_i/T \end{aligned} \tag{14}$$

as $n_j \gg 1$, the $k \ln [n_j/(n_j+1)]$ becomes negligibly small and we get,

$$\ln (g_j/n_j) - \epsilon_j/kT = \ln (g_i/n_i) - \epsilon_i/kT \tag{15}$$

The quantity of j th energy level is independent of that of i th energy level, and as i and j are dummy indices so this condition holds for all particles in all energy levels, and quantity of each side is a constant independent of energy levels.

$$\ln (g_i/n_i) - \epsilon_i/kT = a_{MB} \tag{16}$$

$$(g_i/n_i) = \exp(a_{MB} + \epsilon_i/kT)$$

Rearranging, $n_i = \exp(-a_{MB}) g_i \exp(-\epsilon_i/kT)$ (17)

The relation (17) is **Maxwell-Boltzmann distribution** showing the number of particles in i th energy level at temperature T .

From relation (11) and (13),

$$k \ln n_i/(n_i + g_i - 1) \cdot (n_j + g_j)/(n_j + 1) = (\epsilon_j - \epsilon_i)/T \tag{18}$$

as earlier $\ln (n_i + g_i - 1)/n_i - \epsilon_i/kT = \ln (n_j + g_j)/(n_j + 1) - \epsilon_j/kT$ (19)

Using n_i & $n_j \gg 1$, and the quantity of j th energy level in the righthand side is equal and independent of i th energy level of the lefthand side of the above equation, the i and j are dummy indices so quantity of each side is a constant of energy level. This condition holds for all particles in all energy level following Bose-Einstein distribution or Bosons. From (19),

$$\ln (n_i + g_i)/n_i = a_{BE} + \epsilon_i/kT$$

$$(n_i + g_i)/n_i = \exp(a_{BE} + \epsilon_i/kT)$$

Rearranging, $n_i = g_i/[\exp(a_{BE} + \epsilon_i/kT) - 1]$ (20)

The relation (20) is **Bose-Einstein distribution** showing the number of particles or bosons in i th energy level at temperature T .

From relation (12) and (13),

$$k \ln n_i/(g_i - n_i + 1) \cdot (g_j - n_j)/(n_j + 1) = (\epsilon_j - \epsilon_i)/T \tag{21}$$

Using same arguments for Bose-Einstein distribution, we get

$$(g_i - n_i)/n_i = \exp(a_{FD} + \epsilon_i/T)$$

Rearranging, $n_i = g_i/[\exp(a_{FD} + \epsilon_i/kT) + 1]$ (22)

The relation (22) is **Fermi-Dirac distribution** showing the number of particles or fermions in i th energy level at temperature T .

3. Partition function^{2b}

From relation (17), we get

$$n_i = \exp(-a_{MB}) g_i \exp(-\epsilon_i/kT)$$

$$N = \exp(-a_{MB}) \sum_i g_i \exp(-\epsilon_i/kT)$$

$$\exp(-a_{MB}) = N/z$$

$$z = \sum_i g_i \exp(-\epsilon_i/kT) \tag{23}$$

where z is called the partition function of a particle and Maxwell-Boltzmann distribution is expressed in terms of partition function is,

$$n_i = (N/z) g_i \exp(-\epsilon_i/kT) \tag{24}$$

The fraction of the system in i th energy state is

$$n_i / N = g_i \exp(-\epsilon_i/kT)/z \tag{25}$$

The average energy of a particle using (24) is

$$\begin{aligned} \langle \epsilon \rangle &= \sum_i n_i \epsilon_i / N = \sum_i \epsilon_i g_i \exp(-\epsilon_i/kT)/z \\ &= -(1/z) \partial z / \partial \beta; \quad \text{here } (\beta = 1/kT) \end{aligned} \tag{26}$$

4. Equilibrium condition

From relation (9)

$$S_{eq} = k \ln \prod_r g_r^{n_r} / n_r!$$

With Stirling's approximation $\ln n! = n \ln n - n = n \ln(n/e)$, the above expression becomes

$$S_{eq} = k \sum_r n_r \ln(g_r e / n_r) \tag{27}$$

So, the entropy of a particle in i th energy level is

$$S_i = k \ln(g_i e / n_i) \tag{28}$$

On adding $(k \ln e)$ to both sides of the equation (15), to express the entropy of i th and j th particles, we get

$$\epsilon_i - kT \ln(g_i e / n_i) = \epsilon_i - kT \ln(g_i e / n_i) \tag{29}$$

As argument given to arrive relation (16), we get

$$\epsilon_i - kT \ln(g_i e / n_i) = a_H \tag{30}$$

$$\epsilon_i - TS_i = a_H \tag{31}$$

Which is valid for all particles in all energy levels. Here a_H is the Helmholtz energy of a particle in i th energy level, and it is same for all particles irrespective of the energy level they belong to. Hence it is the **equilibrium condition** of the system.

5. Helmholtz energy, Gibbs energy and chemical potential^{2c}

On adding a_H of equation (30) for all N particles of the system,

$$\begin{aligned} Na_H &= \sum_i n_i \epsilon_i - kT \sum_i n_i \ln(g_i e / n_i) \\ &= E - TS_{eq} = A \end{aligned} \tag{32}$$

Here A is the **Helmholtz energy** of the system.

The change of Helmholtz energy per particle of the system is the chemical potential of a particle in the system.

$$\begin{aligned} (\delta A / \delta N)_{T,V} &= (\delta A / \delta n_r)_{T,V} \cdot (\delta n_r / \delta N)_{T,V} \\ \text{(as } (\delta n_r / \delta N)_{T,V} \text{ is unity),} &= \delta / \delta n_r (\sum_r n_r \epsilon_r - \sum_r n_r kT \ln(g_r e / n_r))_{T,V} \\ &= \epsilon_r - kT \ln(g_r / n_r) = -kT \ln[g_r \exp(-\epsilon_r/kT)] / n_r \\ &= \mu \end{aligned} \tag{33}$$

Using relation (25), $\mu = -kT \ln z / N$

The μ is the **chemical potential** of a particle.

Hence, at constant temperature and volume μ (per particle) = $\mu_0 + kT \ln N$

Generally, the chemical potential is expressed in terms of moles, so

$$\mu \text{ (per mole)} = \mu_0 + RT \ln n \text{ (in moles)} \tag{34}$$

The relation (32) becomes,

$$A = \sum_r n_r \epsilon_r - kT \sum_r n_r \ln (g_r/n_r) - kT \sum_r n_r \ln e$$

$$= \sum_r n_r \mu - NkT$$

Using ideal gas relation ($PV = NkT$), we get

$$A + PV = N\mu = G \tag{35}$$

The G is the **Gibbs energy** of the system.

$$A = \sum_r n_r a_H$$

$$= \sum_r n_r (\epsilon_r - kT \ln (g_r e / n_r))$$

$$= -kT \sum_r n_r \ln (g_r e \exp (-\epsilon_r/kT) / n_r)$$

$$= -kT \sum_r n_r \ln e (z/N)$$

$$= -kT N \ln e (z/N)$$

$$= -kT \ln (z^N/N!) \tag{36}$$

The Helmholtz energy of the system containing N indistinguishable particle.

6. Entropy maximum at equilibrium

At equilibrium the system remains unchanged unless any of the macroscopic conditions such as the volume, temperature, energy and number of particles are changed. The entropy of the system depends on the distribution of particles over the energy levels which remains constant at equilibrium. We have not assumed the entropy at equilibrium is the maximum which is used as the basis of conventional approach of the derivation of statistical distributions, partition functions etc. Let us check whether the entropy at equilibrium used in our derivation is the maximum or not.

If only the distribution at equilibrium is perturbed by transferring one particle from i^{th} to j^{th} energy level and another particle from s^{th} to t^{th} energy level of the system at constant temperature and constant volume and to keep the internal energy E remain constant, we must have

$$(\epsilon_j - \epsilon_i) + (\epsilon_t - \epsilon_s) = 0 \tag{37}$$

The change of the entropy of the deviated state of the system following the above transfer of particles using relation (10) is,

$$\Delta S = (S' - S_{eq})$$

Expressing in terms of entropy of individual particles, we get

$$\Delta S = k \ln (g_j e/n_j) - k \ln (g_i e/n_i) + k \ln (n_j/(n_j + 1))$$

$$+ k \ln (g_t e/n_t) - k \ln (g_s e/n_s) + k \ln (n_t/(n_t + 1))$$

Using condition (29), we get

$$\Delta S = k \ln (n_j/(n_j + 1)) + k \ln (n_t/(n_t + 1))$$

$$< 0 \tag{38}$$

The logarithm of fractions $(n_j/(n_j + 1))$ and $(n_t/(n_t + 1))$ are negative, so any deviation from equilibrium Condition, the entropy becomes less than equilibrium entropy. This condition shows the entropy is the **maximum** at equilibrium.

7. Conclusion

The Clausius inequality relation of entropy change and Boltzmann expression of entropy are enough to develop the three statistical distributions from their respective counting of distinct arrangements or states Ω_{MB} , Ω_{BE} and Ω_{FD} of the system. The partition function and three statistical distributions arrive automatically in the derivation avoiding the calculus of variation and Lagrange undetermined multipliers commonly used for their derivation in statistical thermodynamics. The Helmholtz and Gibbs energies and chemical potential are shown as the equilibrium properties of the system. We hope this derivation using the role of entropy change and the same, using Clausius inequality relation are useful to derive all these relation without any rigorous involvement of calculus of variation.

8. References:

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