

Method of Ensembles: Partition Functions **(Application to M-B Statistics)**



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- In earlier lecture, we have derived the thermodynamical functions of a thermodynamic system in terms of partition function.
- In this lecture, we will be able to understand the followings –
 - N-particle partition function and its thermodynamic relations
 - concept of entropy of mixing (Gibbs paradox)

N-Particle Partition Function and Thermodynamic variables

- Consider a system of N-indistinguishable particles characterised by non-degenerate states whose partition function is given by –

$$Z_N = \sum_{i=1}^N e^{-\beta\varepsilon_i} = \sum (e^{-\beta\varepsilon_1})(e^{-\beta\varepsilon_2})\dots\dots(e^{-\beta\varepsilon_N}) = Z_1.Z_2\dots\dots Z_N$$

$$Z_N = \left(\sum_i \exp(-\beta\varepsilon_i) \right)^N = Z^N \dots\dots\dots(i)$$

- Hence, *N-particle partition function* is given by -

$$Z_N = V^N \left(\frac{mkT}{2\pi\hbar^2} \right)^{3N/2} \dots\dots\dots(ii)$$

taking natural logarithm of eqⁿ. (ii), we get

$$\ln Z_N = N \left[\ln V + \frac{3}{2} \ln(kT) + \frac{3}{2} \ln \left(\frac{m}{2\pi\hbar^2} \right) \right] \dots\dots\dots(iii)$$

Now, for *N-particle partition function*, internal energy of a gas is written as –

$$E = kT^2 \left[\frac{\partial}{\partial T} (\ln Z_N) \right]_{V,N} \dots\dots\dots(iv)$$

from (iii), $E = \frac{3}{2} NkT \dots\dots\dots(v)$

Heat capacity at constant volume is given by -

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = \frac{3}{2} Nk = \frac{3}{2} nR \dots\dots\dots(vi)$$

Pressure exerted by a gas (in terms of *N-particle partition function*) is given by –

$$P = kT \left[\frac{\partial}{\partial V} (\ln Z_N) \right]_{T,N} = \frac{NkT}{V} \dots\dots\dots(vii)$$

from eqⁿ. (v) and (vii), we get

$$P = \frac{2E}{3V} \dots\dots\dots(viii)$$

Helmholtz free energy (in terms of *N-particle partition function*) is given by –

$$F = -kT \ln Z_N = -NkT \ln \left[\frac{V}{h^3} (2\pi mkT)^{3/2} \right] \dots\dots\dots(ix)$$

Entropy of a system (*in terms of N-particle partition function*)

is given by - $S = k \ln Z_N + \frac{E}{T}$ (x)

from eqⁿ. (iii) and (v), we get

$$S = Nk \left[\ln(VT^{3/2}) + \frac{3}{2} \ln k + \frac{3}{2} \ln \left(\frac{m}{2\pi\hbar^2} \right) \right] + \frac{3}{2} Nk$$

$$S = Nk \left[\ln(VT^{3/2}) + \ln \left(\frac{2\pi m k e}{h^2} \right)^{3/2} \right] = Nk \left[\ln(VT^{3/2}) + C \right] \text{(xi)}$$

where, $C = \ln \left(\frac{2\pi m k e}{h^2} \right)^{3/2}$

This gives the entropy of an ideal monoatomic gas.

Entropy of Mixing and Gibbs Paradox

As we know, the partition function of an ideal gas is-

$$Z = \frac{V}{h^3} (2\pi mkT)^{3/2} \dots\dots[1]$$

Entropy of an ideal gas is –

$$S = Nk \ln Z + \frac{3}{2} Nk \dots\dots[2]$$

$$\text{or, } S = Nk \left[\ln V + \frac{3}{2} \ln m + \frac{3}{2} \ln T + A \right] \dots\dots[3]$$

where A is a constant term involving h & k.

The mixing of two different ideal gases is an irreversible process and leads to an increase in entropy. Let us consider two different ideal gases at the same temperature contained in two chambers having volumes V_1 and V_2 and separated by a rigid partition.

1	2
(N_1, V_1, m_1, T)	(N_2, V_2, m_2, T)
S_1	S_2

If the particles of the two systems are different then from eqⁿ. (iii), the entropies of the system 1 and 2 are given by

$$- \quad S_1 = N_1 k \left[\ln V_1 + \frac{3}{2} \ln m_1 + \frac{3}{2} \ln T + A \right] \dots\dots[4]$$

$$S_2 = N_2 k \left[\ln V_2 + \frac{3}{2} \ln m_2 + \frac{3}{2} \ln T + A \right] \dots\dots[5]$$

As entropy is an extensive property so it must satisfy the additive property. If the entropy had shown the additive property and then by removing the partition and thereby allowing the gas molecules to mix freely, the entropy of the joint system would be given as –

$$S_{12} = S_1 + S_2$$

$$S_{12} = N_1 k \left[\ln V_1 + \frac{3}{2} \ln m_1 + \frac{3}{2} \ln T + A \right] + N_2 k \left[\ln V_2 + \frac{3}{2} \ln m_2 + \frac{3}{2} \ln T + A \right] \dots\dots[6]$$

If the *particles* of the two systems are *same* and suppose, $V_1 = V_2 = V$ and $N_1 = N_2 = N$ then, entropy of the combined system would be -

$$S_{12} = 2Nk \left[\ln V + \frac{3}{2} \ln m + \frac{3}{2} \ln T + A \right] \dots\dots[7]$$

- Now, let us suppose that the partition be removed and molecules of the gases are allowed to mix freely resulting in a mixed system having $2N$ particles in a volume $2V$. Therefore, entropy of the mixed system from eqⁿ. (iii) is given by

$$S_{12} = 2Nk \left[\ln 2V + \frac{3}{2} \ln m + \frac{3}{2} \ln T + A \right] \dots\dots[8]$$

$$S_{12} = 2Nk \left[\ln V + \frac{3}{2} \ln m + \frac{3}{2} \ln T + A \right] + 2Nk \ln 2$$

$$S_{12} = S_1 + S_2 + 2Nk \ln 2 \dots\dots\dots[9]$$

which is not the same as eqⁿ. (7) but contains an additional term $2Nk \ln 2$. This indicates that by mixing two different gases, each containing same number of molecules N , by removing the partition, the entropy of the system increases by an amount $2Nk \ln 2$. This additional entropy is known as *entropy of mixing or Gibbs paradox*.

Thus, eqⁿ. (iii) of entropy gives paradoxical result.

Gibbs Paradox: Let us consider that the same monoatomic gas is put in two chambers separated by a rigid partition. Therefore, entropy of mixing for self-diffusion to be zero. But even for self-mixing, it predicts the same increase in entropy as for intermixing of two different gases.

➤ The derivation of eqⁿ. (ix) does not depend on the identity of a gas or its molecules.

Resolution of the Paradox: Gibbs resolved this paradox by considering the *two systems as same* and hence, the gas molecules completely *identical and indistinguishable*. Hence, if two systems containing same number N of identical particles are mixed by removing a partition.

In 1911, Sackür suggested that if the thermodynamic probability (of M-B distribution law) is divided by $N!$ then Gibbs paradox could be resolved. Thus, thermodynamic probability should be modified to

$$W = \prod_i \frac{g_i^{n_i}}{n_i!} \dots\dots\dots[10]$$

Taking natural logarithms and apply Stirling's approx., we get

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

Entropy is -

$$S^{corr} = k \ln W = k \left[N + \sum_i n_i \ln \left(\frac{g_i}{n_i} \right) \right]$$

$$\therefore \frac{n_i}{g_i} = \frac{N}{Z} e^{-\beta \epsilon_i}$$

Therefore, $S^{corr} = Nk[\ln Z - \ln N + 1] + \frac{E}{T}$ [11]

For a gas of N molecules, the expression for correct entropy can be further written in terms of N-particle partition function (as from eqⁿ. (iii)). Now, eqⁿ. (11) becomes –

$$S_N^{corr} = k \ln Z_N = Nk \left[\ln V + \frac{3}{2} \ln(kT) + \frac{3}{2} \ln \left(\frac{m}{2\pi\hbar^2} \right) - \ln N + 1 \right] + \frac{3}{2} Nk$$

$$S_N^{corr} = Nk \left[\ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln(kT) + \frac{3}{2} \ln \left(\frac{m}{2\pi\hbar^2} \right) + \frac{5}{2} \right]$$

$$S_N^{corr} = Nk \left[\ln \left(\frac{VT^{3/2}}{N} \right) + \ln \left\{ \left(\frac{2\pi mk}{h^2} \right)^{3/2} e^{5/2} \right\} \right]$$

$$S_N^{corr} = Nk \left[\ln \left(\frac{VT^{3/2}}{N} \right) + C_0 \right] \quad \dots\dots\dots[12]$$

where

$$C_0 = \ln \left\{ \left(\frac{2\pi mk}{h^2} \right)^{3/2} e^{5/2} \right\}$$

or,

$$S_N^{corr} = Nk \left[\ln \left(\frac{V}{N\lambda_{dB}^3} \right) + \frac{5}{2} \right] \quad \dots\dots\dots[13]$$

where $\lambda_{dB} = \frac{h}{\sqrt{2\pi mkT}}$ (Thermal de-Broglie wavelength)

This eqⁿ. (13) is known as **Sackür-Tetrode equation** and it gives the absolute value of entropy of a monoatomic gas. Accounting the *indistinguishability* nature of the particles of an ideal monoatomic gas, the above eqⁿ. gives resolution to Gibbs paradox.

References: Further Readings

1. *Statistical Mechanics* by R.K. Pathria
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3. *Statistical Mechanics* by K. Huang
4. *Statistical Mechanics* by B.K. Agrawal and M. Eisner
5. *Statistical Mechanics* by Satya Prakash

Thank You

**For any questions/doubts/suggestions and submission of
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