Statistical review of entropy

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Abstract:

Entropy is a measurement of disorder in any thermodynamic system.Clausius introduced the concept of entropy in mid nineteen century and since then it has been continuously enriched our concepts regarding different branches of science. Concept of thermodynamic entropy was introduced by L.Boltzmann, and according to him thermodynamic entropy is directly proportional to logarithm of the number of microstates of the system. In this research paper we have discussed applications of this resultin Maxwell Boltzmann, Bose Einstein and Fermi Dirac statistics. In statistical mechanics Helmholtz function, entropy and partition function are directly linked together with different relations. Using this concept we have evaluated partition function, Helmholtz function and entropy for quantum mechanical harmonic oscillator, classical harmonic oscillator, paramagnetic and paraelectric substances, ideal and relativistic classical gas, black body radiation, monoatomic gasses in different dimensions, rotational motion etc. A brief analysis of entropy with the help of Gibbs free energy and entropy in grand canonical ensemble is also done..

Keywords: Entropy, Helmholtz function, Gibbs free energy, classical gas etc

Introduction:

Entropy was initially introduced by Clausius about 165 years ago and it is highly useful for the researchers in many different scientific discipline. In statistical mechanics behaviour of any thermodynamic system depends upon their constituent particles, for a particular particle in statistical classical mechanics, microstates of any system can be defined by position and momentum of all the particles of the system. Now if a system consist N , number of particles in the system then microstate of system can be specified by 3N position co-ordinates q_1,q_2,q_3………q_{3N} and 3N momentum co-ordinates p_1,p_2,p_3………p_{3N}. obviously 6N dimension is required to completely described the system. This type of 6N dimensional space is known to be phase space. Phase point(q_j,p_j) are said to be representative point of the given system.

State of a particle in phase space is then given by specifying that its position co-ordinate lie in the interval between q and q+δq , and at the same instant its momentum co-ordinates lies in the interval between p and p+δp , it means phase space is divided into very small phase cells of size δpδq here each cell have the same size and each cell represents a different states of the particle.

According to Heisenberg uncertainty principle (HUP) $\Delta q\Delta p\sim$h here h is planck constant and having the dimension of joule-sec. Δq represents uncertainty in the measurement of position and Δp is the corresponding uncertainty in the measurement of the momentum. HUP itself ensure that phase space should be divided into subparts having the volume h of a particular phase cell. Therefore two dimensional volume of a particular phase cell will be of the order of h (planck constant). In a 2f dimensional space volume of a particular phase cell will be h^f . This result ensure that in two dimensional phase space, volume of a particular phase cell will be order of h. Similarly in four dimensional phase space and six dimensional space volume of a corresponding phase cell will be of the order of h^2 and h^3 respectively. In mathematical form we can represent volume of a phase cell

$\Delta x\Delta p_x\sim$h (joule-sec) two dimension phase cell volume

$\Delta x\Delta p_x\Delta y\Delta p_y\sim h^2$ (joule-sec)^2 four dimension phase cell volume

$\Delta x\Delta p_x\Delta y\Delta p_y\Delta z\Delta p_z \sim h^3$(joule-sec)^3 six dimension phase cell volume

From modern quantum physics we know that state of a system is described by spatial parts and spin parts. Due to this volume of phase space also depends upon spatial or position- momentum part and it also depends upon total spin states. For a particular system which consist many particles and each individual particle have spin s then for such particle magnetic spin quantum number m_s have the value lies between -s to +s , so total spin state is equal to $\sum_{-s}^{+s} m_s$= (2s+1)=γ values.

According to Maxwell Boltzmann statistics, no of particles in rt^h state depends upon density of states g_r and energy ε_r and temperature T of any thermodynamic system

$$n_r = A\, g_r(\varepsilon_r)e^{-\beta\varepsilon_r}$$

Or $$\frac{n_r}{g_r} = A\, e^{-\beta\varepsilon_r}$$

$$f_{MB} = A\, e^{-\beta\varepsilon_r}$$

$$\sum_r f_{MB} = 1$$

$$\sum_r A\, e^{-\beta\varepsilon_r} = 1$$

$$A = \frac{1}{\sum_r e^{-\beta\varepsilon_r}} = \frac{1}{Z}$$

Z is the partition function or sum over state of the system.

Suppose the level of energy ε_r be degenerate having degeneracy $g_r(\varepsilon_r)$, then partition function

$$Z = \sum_r g_r(\varepsilon_r)e^{-\beta\varepsilon_r}$$

The probability of a microstate as a function of its energy is given by Boltzmann distribution

$P_r = \frac{e^{\frac{-\varepsilon_r}{kT}}}{\sum_r e^{\frac{-\varepsilon_r}{kT}}} = \frac{e^{\frac{-\varepsilon_r}{kT}}}{Z}$ where Z is the partition function of the system and T is the temperature and k is the Boltzmann constant.

According to Gibbs entropy relation the entropy of a thermodynamic system is linked to probability distribution function $S = -k\sum_r P_r log P_r$

now P_r is directly linked to W where W is the number of microstate of the system

$$P_r \propto \frac{1}{W}$$

$$S = -k\sum_{r=1}^{W} P_r log P_r$$

$$S = -k\sum_{r=1}^{W}\frac{1}{W}log\frac{1}{W} = \text{klogW}$$

This expression is said to be Boltzmann Planck equation

Boltzmann Planck equation is also applicable for more than one macrostate and then entropy of a macrostate i $S_i = klogW_i$ where W_i = number of microstates corresponding to that microstates.

In terms of probability internal energy of any thermodynamic system is $U = \sum_r P_r \, \varepsilon_r$ where P_r is the probability of finding the particle in microstate r and ε_r is the energy of particle in corresponding rth state.

Now from the Helmholtz function F= U-TS = -kTlogZ so S= klogZ+$\frac{U}{T}$

$$dF= dU-TdS-SdT= dQ- dW--TdS-SdT$$

$$dF= TdS-PdV-TdS-SdT$$

$$dF= -PdV-SdT$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$\text{Entropy } S = -\left(\frac{\partial F}{\partial T}\right)_V$$

Result and Discussion

1. **Analysis of Maxwell Boltzmann, Bose Einstein and Fermi Dirac statistics:**

   Number of distinguishable ways, W in MB statistics can be described as $W = \prod_i^N \frac{{g_i}^{n_i}}{n_i!}$ Where g_i are the number of various states in which particle can be filled and n_i are the number of particles. Number of distinguishable ways, W in BE statistics can be described as $W = \prod_i^N \frac{(n_i+g_i-1)!}{n_i!(g_i-1)!}$ Where g_i are the number of various states in which particle can be filled and n_i are the number of particles. Number of distinguishable ways, W in FD statistics can be described as $W = \prod_i^N \frac{g_i!}{n_i!(g_{i-}n_i)!}$ Where g_i are the number of various states in which particle can be filled and n_i are the number of particles. Then using the expression S=klogW we can easily evaluate entropy of the system in various cases.

2. **Analysis in the case of Grand canonical ensemble:**

$$Z(\mu, T) = \sum_r exp[(\mu N_r - E_r)\beta]$$

$$P_r = \frac{exp[(\mu N_r - E_r)\beta]}{Z(\mu, T)}$$

   Now entropy in terms of probability P_r is given by $S = -k \sum_r P_r log P_r$
   On solving we have $S = -k\mu\beta\langle N\rangle + k\beta\langle E\rangle + klogZ(\mu, T)$

$$S = \frac{\langle E\rangle}{T} - \frac{\mu\langle N\rangle}{T} + klogZ(\mu, T)$$

   This is the expression of entropy. where $\langle E\rangle$ is average energy and $\langle N\rangle$ is the average number of particle and μ is the chemical potential.

3. **Analysis of a gas through Gibbs free energy:**

For a monoatomic gas Gibbs free energy which is the function of pressure and temperature can be described as $G(P.T) = RT \log\left[\frac{aP}{(RT)^{\frac{5}{2}}}\right]$ where a and R are the constants then the entropy of the system S= $-\left[\frac{\partial G}{\partial T}\right]_P$ = $\frac{5}{2}R - R\log\left[\frac{aP}{(RT)^{\frac{5}{2}}}\right]$

This expression shows that entropy depends upon pressure P and temperature T and when temperature T increases and pressure P decreases then entropy increases and vice versa.

4. Analysis of quantum mechanical harmonic oscillator:

According to quantum mechanics the possible energy levels of harmonic oscillator can be described as $\varepsilon_n = \left(n+\frac{1}{2}\right)\hbar\omega$, where n is the quantum number and ω is the angular frequency which depends upon force constant k and mass m.

$$\omega=\sqrt{\frac{k}{m}}$$

now from the expression of partition function we have

$$Z = \sum_{n=0}^{\infty} e^{-\beta\varepsilon_n} = \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega} = e^{\frac{-\beta\hbar\omega}{2}}\ \frac{1}{1-e^{-\beta\hbar\omega}}$$

$$Z= \left\{2sinh\left(\frac{\beta\hbar\omega}{2}\right)\right\}^{-1}$$

Now the partition function for N harmonic oscillator

$$Z= \left\{2sinh\left(\frac{\beta\hbar\omega}{2}\right)\right\}^{-N}$$

Now the Helmholtz free energy of the system

$$F= \text{NkTlog}\left[2sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]$$

Then entropy of the system would be

$$S= \text{Nk}\left[\frac{\beta\hbar\omega}{2}coth\frac{\beta\hbar\omega}{2} - log\left[2sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]\right]$$

This expression shows that entropy of quantum mechanical harmonic oscillator depends upon total number of harmonic oscillator N, temperature T and angular frequency ω.

5. Analysis of a free non relativistic particle confined in a cubic box:

From the quantum mechanics we know that energy eigen value for free non relativistic particle can be expressed as

$\varepsilon= \left({n_x}^2 + {n_y}^2 + {n_z}^2\right)\frac{h^2}{8mL^2}$

where ε = energy, n_x, n_y, n_z are the positive integer, L is the length of the box and h is the planck constant.

This can be expressed as $\sum_{r=1}^{3N} {n_r}^2 = \frac{8mV^{\frac{2}{3}}E}{h^2} = constant$

Entropy will be depends upon number of particle, volume of the cubic box and energy E so we have

$S(N,V,E) \equiv S\left(N, V^{\frac{2}{3}}E\right)$

For a reversible adiabatic process entropy remains to be constant so we have $V^{\frac{2}{3}}E=$ constant and pressure P = $-\left[\frac{\partial E}{\partial V}\right]_{N,S} = \frac{2}{3}\frac{E}{V}$ here pressur is equal to two third of its energy density.

6. Analysis of Classical Harmonic oscillator in various dimensions :

Energy of classical harmonic oscillator is equal to the sum of kinetic energy and potential energy ε $= \frac{p_x^2}{2m} + \frac{1}{2}kx^2$

From the definition of partition function we have

$$Z = \sum_r g_r(\varepsilon_r)e^{-\beta\varepsilon_r}$$

Now using the concept of phase space and taking the limit of x and p_x from $-\infty$ $to + \infty$

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{dx\,dp_x}{h}e^{-\beta\left[\frac{p_x^2}{2m}+\frac{1}{2}kx^2\right]}$$

On solving we get

$$Z = \left(\frac{kT}{\hbar\omega_x}\right) \qquad \text{1D}$$

For N oscillator system partition function would be

$$Z_N = (\beta\hbar\omega)^{-N}$$

$$\text{Here } \omega_x = \sqrt{\frac{k_x}{m}} = \omega$$

$$\text{Now the Helmholtz energy of the system F} = -\text{kTlog}(\beta\hbar\omega)^{-N} = \text{NkTlog}\left(\frac{\hbar\omega}{kT}\right)$$

$$\text{Entropy S} = -\left[\frac{\partial F}{\partial T}\right]_{N,V} = \text{Nk}\left[log\left(\frac{kT}{\hbar\omega}\right)+1\right]$$

This expression shows that entropy depends upon the number of harmonic oscillator, temperature T and frequency ω and it increases when number of harmonic oscillator is increased and temperature of the system is increased and frequency of oscillation is decreased.

Partition function obey the multiplicative property in different direction so for Anisotropic 2D harmonic oscillator we have Z= Z_xZ_y

$$Z = \left(\frac{kT}{\hbar\omega_x}\right)\left(\frac{kT}{\hbar\omega_y}\right) \qquad \text{Anisotropic 2D}$$

$$\text{Here } \omega_x = \sqrt{\frac{k_x}{m}},\ \omega_y = \sqrt{\frac{k_y}{m}}$$

$$\text{And } Z = \left(\frac{kT}{\hbar\omega}\right)^2 \text{ Isotropic 2D}$$

$$\text{here } \omega_x = \omega_y = \omega$$

$$\text{Now the Helmholtz energy of the system F} = -\text{kTlog}(\beta\hbar\omega)^{-2N} = \text{2NkTlog}\left(\frac{\hbar\omega}{kT}\right)$$

$$\text{Entropy S} = -\left[\frac{\partial F}{\partial T}\right]_{N,V} = \text{2Nk}\left[log\left(\frac{kT}{\hbar\omega}\right)+1\right]$$

This expression shows that entropy depends upon the number of harmonic oscillator, temperature T and frequency ω and it increases when number of harmonic oscillator is increased and temperature of the system is increased and frequency of oscillation is decreased.

for 3D harmonic oscillator partition function Z= $Z_x Z_y Z_z$

$$= \left(\frac{kT}{\hbar\omega_x}\right)\left(\frac{kT}{\hbar\omega_y}\right)\left(\frac{kT}{\hbar\omega_z}\right) \qquad \text{Anisotropic 3D}$$

$$\text{And Z=} \left(\frac{kT}{\hbar\omega}\right)^3 \text{ Isotropic 3D}$$

$$\text{here } \omega_x = \omega_y = \omega_z = \omega$$

$$\text{Now the Helmholtz energy of the system F= -kTlog}(\beta\hbar\omega)^{-3N} = \text{3NkTlog}\left(\frac{\hbar\omega}{kT}\right)$$

$$\text{Entropy S=} -\left[\frac{\partial F}{\partial T}\right]_{N,V} = \text{3Nk}\left[log\left(\frac{kT}{\hbar\omega}\right) + 1\right]$$

This expression shows that entropy depends upon the number of harmonic oscillator, temperature T and frequency ω and it increases when number of harmonic oscillator is increased and temperature of the system is increased and frequency of oscillation is decreased.

7. Analysis of paramagnetic and paraelectric substance :

In the paramagnetic substance when the magnetic moment of the atom parallel to be B then energy of the atomic magnet In the up position

$$\varepsilon_1 = -\mu_B B$$

In the paramagnetic substance when the magnetic moment of the atom antiparallel to be B then energy of the atomic magnet In the down position

$$\varepsilon_2 = +\mu_B B$$

Now the partition function in such a case Z= $e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2}$

$$= e^{+\beta\mu_B B} + e^{-\beta\mu_B B}$$

$$= 2\cosh(\beta\mu_B B)$$

For N number of dipoles partition function of system can be written as Z=$\left(2\cosh(\beta\mu_B B)\right)^N$

Now the Helmholtz energy of the system F= - NkTlog[2cosh $(\beta\mu_B B)$]

$$\text{Entropy S=} -\left[\frac{\partial F}{\partial T}\right]_{N,V} = \text{Nk}\left[log\{2\cosh(\beta\mu_B B)\} - \frac{\mu_B B}{kT} tanh\left(\frac{\mu_B B}{kT}\right)\right]$$

This expression shows that entropy depends upon the temperature T and magnetic field B and number of dipoles N and value of entropy increases when number of dipoles is increased and temperature of the system is increased and value of applied magnetic field B is decreased.

This expression is valid only when magnetic moment of the atom is parallel and antiparallel to B.

In the paraelectric substance when the dipole moment of the atom parallel to be E then energy of the electric dipole In the up position

$$\varepsilon_1 = -pE$$

In the paraelectric substance when the dipole moment of the atom antiparallel to be E then energy of the electric dipole In the down position

$$\varepsilon_2 = +pE$$

Now the partition function in such a case Z= $e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2}$

$$= e^{\beta pE} + e^{-\beta pE}$$

$$= 2\cosh(\beta pE)$$

For N number of dipoles partition function of system can be written as Z=$\left(2\cosh(\beta pE)\right)^N$

Now the Helmholtz energy of the system F= - NkTlog[2cosh (βpE)]

$$\text{Entropy S}= -\left[\frac{\partial F}{\partial T}\right]_{N,V} = \text{Nk}\left[log\{2\cosh(\beta pE)\} - \frac{pE}{kT}tanh\left(\frac{pE}{kT}\right)\right]$$

This expression shows that entropy depends upon the temperature T and electric field E and number of dipoles N and value of entropy increases when number of dipoles is increased and temperature of the system is increased and value of applied electric field E is decreased.

8. Analysis of ideal classical gas :

For Cubic box (3D) Z= $\frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}}$ here Here V= L^3= volume of cubic

If there are N number of particles and molecules are distinguishable then partition function of such ideal classical gas

$$Z= \frac{V^N}{h^{3N}}(2\pi mkT)^{\frac{3N}{2}}$$

If there are N number of particles and molecules are indistinguishable then partition function of such ideal classical gas

$$Z= \frac{1}{N!}\frac{V^N}{h^{3N}}(2\pi mkT)^{\frac{3N}{2}}$$

From the Helmholtz function and partition function relation we have

$$F = -kT \log Z$$

$$= \text{NkT}\left[log\left(\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)\right)^{\frac{3}{2}} - 1\right]$$

Evaluation of Entropy:

Partition function of ideal gas when molecules are distinguishable in nature

$$Z= \left(\frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}}\right)^N$$

From the relation F= -kTlogZ= E-TS

$$\text{We have S= klogZ} + \frac{E}{T} = \text{Nk log}\left(\frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}}\right) + \frac{3}{2}Nk$$

$$\text{S= Nk}\left[\log V + \frac{3}{2}log\left(\frac{2\pi mkT}{h^2}\right) + \frac{3}{2}\right]$$

Gibbs Paradox: consider two containers having the same volume V , both the container consist N number of atoms behaving as a ideal classical monoatomic gas and they are separated by a partition. Both gases are at the same temperature T. when removal of partition takes place then the entropy of the gas increases.

Using above relation entropy of initial case

$$S_i= 2\text{Nk} \left[\log V + \frac{3}{2} log \left(\frac{2\pi mkT}{h^2}\right) + \frac{3}{2}\right]$$

After removal of the partition system consist 2N number of atoms and occupied volume 2V and gas consist a temperature T therefore final entropy of the system becomes

$$S_f= 2\text{Nk} \left[\log 2V + \frac{3}{2} log \left(\frac{2\pi mkT}{h^2}\right) + \frac{3}{2}\right]$$

Therefore we have $S_f - S_i$ = 2Nklog2

It means entropy is not behaving as an extensive parameter. This is said to be Gibbs Paradox. Since we have the same gas in both the containers, removal of partition is a reversible process so entropy should not be change. When the gases in the container have the different nature then removal of partition is an irreversible process and so entropy must be increased. This paradox can be understandable when molecules of the gas should not assume to be distinguishable because order of the molecules (10^{23}) is very large and such molecules are continuously in motion and changing there position continuously. Since molecules are very near by to each other so we should consider molecules of classical gas as an indistinguishable and partition function should be divided by N!.

$$\text{Z}= \frac{1}{N!}\left(\frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}}\right)^N$$

Helmholtz function F = -kTlogZ

$$\text{F}= -\text{kTlog}\frac{1}{N!}\left(\frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}}\right)^N$$

For very large value of N

logN! = NlogN-N (Stirling approximation)

$$\text{Entropy S} = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

On solving

$$\text{S(N,V,T)} = \text{Nk}\left[log\frac{V}{N} + \frac{3}{2} log \left(\frac{2\pi mkT}{h^2}\right) + \frac{5}{2}\right]$$

This expression is said to be Sackur Tetrode equation and this expression successfully explain the Gibbs Paradox.

Removal of Gibbs Paradox: consider two containers having the same volume V , both the container consist N number of atoms behaving as a ideal classical monoatomic gas and they are separated by a partition. Both gases are at the same temperature T. when removal of partition takes place then the entropy of the gas remains to be same.

Using above relation entropy of initial case

$$S_i= 2\text{Nk} \left[\log\frac{2V}{2N} + \frac{3}{2} log \left(\frac{2\pi mkT}{h^2}\right) + \frac{5}{2}\right]$$

After removal of the partition system consist 2N number of atoms and occupied volume 2V and gas consist a temperature T therefore final entropy of the system becomes

$$S_f = 2\mathrm{Nk}\left[\log\frac{2V}{2N} + \frac{3}{2}\,log\left(\frac{2\pi mkT}{h^2}\right) + \frac{5}{2}\right]$$

Therefore we have $S_f = S_i$

It means entropy is behaving as an extensive parameter. This is said to be Removal of Gibbs Paradox.

9. Analysis of relativistic gas:

Now for the relativistic classical gas energy momentum relation E=pc

$$\boldsymbol{Z} = \frac{1}{N!}\frac{V^N}{h^{3N}}\left[\int_0^\infty e^{-\beta cp}\,(4\pi p^2 dp)\right]^N$$ on solving we get

$$Z = \frac{1}{N!}\left[8\pi V\left(\frac{kT}{hc}\right)^3\right]^N$$

Helmholtz function corresponding to relativistic classical gas F= - kTlogZ

$$= \quad \text{-kTlog}\,\frac{1}{N!}\left[8\pi V\left(\frac{kT}{hc}\right)^3\right]^N$$

$$\text{Entropy S} = -\left[\frac{\partial F}{\partial T}\right]_{N,V} = \text{Nklog}\frac{1}{N!}\left[8\pi V\left(\frac{kT}{hc}\right)^3\right]^N + 3Nk$$

This expression shows that entropy of the relativistic gas depends upon number of molecules in the gas, volume V of the container and temperature T and it increases when number of molecules in the gas, volume V of the container and temperature T increases and vice versa.

10. Analysis of black body radiation:

Since the photon do not interact so chemical potential μ=0
Grand thermodynamic potential of the system in this case would be

$$\text{F} = \text{-kT}\int_0^\infty log\left(1 - e^{\frac{-h\nu}{kT}}\right)\frac{8\pi V\nu^2 d\nu}{kT}$$

On solving above expression we have

$$\text{F} = -\,\frac{8\pi^5 V(kT)^4}{45(hc)^3}$$

$$\text{Entropy S} = -\left[\frac{\partial F}{\partial T}\right]_{N,V} = \frac{32\pi^5 Vk^4T^3}{45(hc)^3}$$

This expression shows that entropy of the black body radiation directly depends upon volume V of the container and third power of temperature T.

11. Analysis of 1D,2D,3D and DD monoatomic ideal gas:

From the expression Z= $\sum_r g_r(\varepsilon_r)e^{-\beta\varepsilon_r}$

$$\text{Z} = \iint \frac{dx\,dp_x}{h}\,e^{-\beta\frac{p_x^2}{2m}}$$

Now using limit of x and p_x from $-\infty\ to + \infty$ solving we get

$$\text{Zx} = \frac{L_x}{h}\,(2\pi mkT)^{\frac{1}{2}} \qquad \text{Partition function in 1D box}$$

For Rectangular box (2D) Z= Zx Zy

$$=\frac{L_x}{h}(2\pi mkT)^{\frac{1}{2}}\frac{L_y}{h}(2\pi mkT)^{\frac{1}{2}}=\frac{A}{h^2}\ (2\pi mkT)$$

Here A= L_xL_y= area of rectangle box

For Square box (2D) Z= $\frac{L}{h}(2\pi mkT)^{\frac{1}{2}}\frac{L}{h}(2\pi mkT)^{\frac{1}{2}}=\frac{A}{h^2}\ (2\pi mkT)$

Here A= L^2= Area of square box

For Cuboid box (3D) Z= Zx Zy Z_Z

$$=\frac{L_x}{h}(2\pi mkT)^{\frac{1}{2}}\frac{L_y}{h}(2\pi mkT)^{\frac{1}{2}}\frac{L_Z}{h}(2\pi mkT)^{\frac{1}{2}}$$

=$\frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}}$ here Here V=$L_xL_yL_z$ = volume of cuboid box

For Cubic box (3D) Z= $\frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}}$ here Here V= L^3= volume of cubic boxd

From symmetry we have

For D dimensional box Z = $\frac{L^D}{h^D}(2\pi mkT)^{\frac{D}{2}}$

Table 1.1:

Dimension	Partition Function Z
1D	$\frac{L_x}{h}(2\pi mkT)^{\frac{1}{2}}$
2D	$\frac{A}{h^2}\ (2\pi mkT)^{\frac{2}{2}}$
3D	$\frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}}$
DD	$\frac{L^D}{h^D}(2\pi mkT)^{\frac{D}{2}}$

$$F^D = -NkT\ logZ^D$$

$$\mathrm{E^D}=\mathrm{Nk}T^2\frac{\partial}{\partial T}logZ^D = \mathrm{Nk}T^2\frac{\partial}{\partial T}\log\frac{L^D}{h^D}(2\pi mkT)^{\frac{D}{2}}=\frac{D}{2}Nk_BT$$

EntropyS = klogZ+$\frac{E}{T}$

Table 1.2:

Dimension	Entropy S
1D	$S^1 = Nk_B\left[log\frac{L^1}{h^1}(2\pi mkT)^{\frac{1}{2}}+\frac{1}{2}\right]$
2D	$S^2 = Nk_B\left[log\frac{L^2}{h^2}(2\pi mkT)^{\frac{2}{2}}+\frac{2}{2}\right]$
3D	$S^3 = Nk_B\left[log\frac{L^3}{h^3}(2\pi mkT)^{\frac{3}{2}}+\frac{3}{2}\right]$
DD	$S^D = Nk_B\left[log\frac{L^D}{h^D}(2\pi mkT)^{\frac{D}{2}}+\frac{D}{2}\right]$

This expression shows that entropy of the 1D,2D,3D and DD monoatomic gas depends upon number of molecules N length of the box and temperature T and they strongly depends upon dimension D of the box.

12. Analysis of of rotational motion:

A diatomic molecule has only 2 degree of freedom of rotation therefore rotational partition function can be expressed as

$$Z = \frac{1}{h^2}\iint\iint e^{\frac{-\varepsilon(p,q)}{kT}} d\theta\, d\Phi dp_\theta dp_\Phi$$

Where θ,Φ are spherical polar coordinates.

$$\varepsilon(p,q) = \frac{1}{2I}\left(P_\theta^2 + \frac{P_\Phi^2}{sin^2\theta}\right)$$

$$Z = \frac{1}{h^2}\int_0^\pi d\theta \int_0^{2\pi} d\Phi \int_{-\infty}^{+\infty} e^{\frac{-p_\theta^2}{2kT}}\ dp_\theta \int_{-\infty}^{+\infty} e^{\frac{-p_\Phi^2}{2IkT}} sin^2\theta\ \ dp_\Phi$$

On solving, we get

$$Z = \frac{8\pi^2 IkT}{h^2}$$

Therefore Helmholtz function for rotational motion would be F= -kTlogZ

$= -\text{kTlog}\,\frac{8\pi^2 IkT}{h^2}$

$$\text{Entropy S} = -\left[\frac{\partial F}{\partial T}\right]_{N,V} = \text{k logZ} + \frac{E}{T} = -\text{k}\sum_r P_r log P_r$$

$$\text{S} = \text{klog}\frac{8\pi^2 IkT}{h^2} + k$$

And partition function for N diatomic molecule will be $\left(\frac{8\pi^2 IkT}{h^2}\right)^N$

And then helmholtz function F= -NkTlog $\frac{8\pi^2 IkT}{h^2}$

For N diatomic molecule entropy will be S_N=N klog$\frac{8\pi^2 IkT}{h^2} + Nk$

This expression shows that entropy for diatomic molecule depends upon total number of molecules N, moment of inertia I and temperature T and it increases when total number of molecules N, moment of inertia I and temperature T increases and vice versa.

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