PHYS 3014: Statistical Mechanics

Lecture Notes
Part 1

Microcanonical Ensemble : Classical Gas

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Classical Ideal Gas

Consider a classical ideal gas composed of monoatomic molecules. The volume of the system be V.

The no. of ways each particle of the system can be in the volume V must be proportional to V.

So the no. of microstates of the system depends on the volume V of the system.

In the absence of spatial correlations among the particles of the system, the total no. of ways in which N particles can be distributed will be equal to the product of the no. of ways in which the individual particles can be accomodated in the same space independently.

With N and E fixed, the no. of microstates $\Omega(N, E, V)$ of the system

$$\Omega(N, E, V) \propto V^N$$

We have $S(N, E, V) = K \ln \Omega$

and $\left(\frac{\partial S}{\partial V}\right)_{N, E} = \frac{P}{T}$

$$\therefore \quad S(N, E, V) = N K \ln V + F(N, E)$$

$$\therefore \quad \frac{P}{T} = K \frac{N}{V}, \quad K = \text{Boltzmann Constant.}$$

If there are n moles of gas, then

$$N = n N_A \quad , \quad N_A = \text{Avogadro Number}$$

$$\therefore \quad \frac{P}{T} = K \frac{n N_A}{V}$$

$$= n \frac{R}{V} \qquad\qquad R = K N_A$$

or, $$\boxed{PV = nRT}$$

For any classical system composed of non-interacting particles, ideal gas law holds.

The macroscopic conditions of the system are N and E constant. So we have to find the total nu. of ways satisfying the condition

$$\sum_{r=1}^{3N} \epsilon_r = E$$

E_r is the energy associated with the various degrees of freedom of N-particles. Ω also depends on the spectrum of values E_r can assume. E_r depends on V and so Ω also depends on V.

We know that the energy eigen values for a free non-relativistic particle confined in a cubical potential box of side L ($V = L^3$) is given by

$$E(n_x, n_y, n_z) = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)$$

potential inside box is zero and outside box is infinite. n_x, n_y, n_z are non-zero positive integers.

$\therefore$ the no. of distinct eigen functions i.e microstates for a particle having energy ϵ will be equal to the no. of independent tive integral solutions of the equation

$$n_x^2 + n_y^2 + n_z^2 = \frac{8 m V^{2/3}}{h^2} \epsilon$$

clearly for one particle, this no. will be $\Omega(1, \epsilon, V)$.

Therefore, for N particles having total energy E, the total no. of microstates $\Omega(N, E, V)$ will be equal to the independent positive integral solution of

$$\sum_{r=1}^{3N} n_r^2 = \frac{8 m V^{2/3}}{h^2} E \ ,$$

m = mass of particle.
h = Planck const.

For a given value of N, E and V, there will be many sets of values of integers which satisfy this equation. Each such choice defines a specific microstate. All such microstates belong to the same macrostate represented by N, E and V.

$\Omega(N, E, V)$ depend on V and E only through $V^{2/3}E$. So

$\Omega(N, E, V)$ can be written as $\Omega(N, V^{2/3}E)$.

$\Rightarrow$ $S(E, V, N)$ can be written as $S(V^{2/3}E, N)$

or, $$EV^{2/3} = f(S, N)$$

For reversible adiabatic process i.e isentropic process, S and N remain constant.

$$V^{2/3} E = \text{Constant}$$

$$\therefore \quad P = -\left(\frac{\partial E}{\partial V}\right)_{N,S}$$

or $$\boxed{P = \frac{2}{3}\frac{E}{V}}$$

the pressure of a system of non-relativistic non-interacting particles is equal to two-third of its energy density.

Again we now have $PV^{5/3} = \text{Constant}$.

ideal gas equation for adiabatic reversible process or reversible isentropic process.

Calculation of $\Omega(N, V, E)$

The number $\Omega(N, V, E)$ must be equal to the no of positive integral lattice points lying on the surface of a 3N dimensional sphere of radius $\sqrt{\frac{8mV^{2/3}E}{h^2}}$.

* volume of n-dimensional sphere of radius R $= \frac{\pi^{n/2}}{\Gamma\left(\frac{n}{2}+1\right)} R^n = \frac{\pi^{n/2} R^n}{\lfloor n/2}$

* surface of n-dimensional sphere $= \frac{2\pi^{n/2}}{\Gamma\left(\frac{n}{2}\right)} R^{n-1}$

Now the no. of microstates of a given system characterized by the macroscopic condition N and V constant but energy less than or equal to

E is

$$\Sigma(E,V,N) = \sum_{E' \leq E} \Omega(N,V,E')$$

This is irregular with E' but will be smoother than Ω. The no. must be equal to the volume of positive compartment of a 3N-dimensional sphere of radius $\sqrt{\frac{8mV^{2/3}E}{h^2}}$ as energy $E \longrightarrow \infty$.

$$\therefore \quad \Sigma(E,V,N) \simeq \left(\frac{1}{2}\right)^{3N} \frac{\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}+1\right)} \left(\frac{8mV^{2/3}E}{h^2}\right)^{\frac{3N}{2}}$$

$$\simeq \left(\frac{V}{h^3}\right)^N \frac{(2\pi m E)^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}+1\right)}$$

or, $$\ln \Sigma(E,V,N) \simeq N \ln\left[\frac{V}{h^3}(2m\pi E)^{3/2}\right] - \ln \left\lfloor \frac{3N}{2} \right.$$

$$\simeq N \ln\left[\frac{V}{h^3}(2\pi m E)^{3/2}\right] - \frac{3N}{2}\ln\left(\frac{3N}{2}\right) + \frac{3N}{2}$$

$$\simeq N \ln\left[\frac{V}{h^3}\left(\frac{4\pi m E}{3N}\right)^{3/2}\right] + \frac{3}{2}N$$

Due to irregular nature of $\Omega(E, V, N)$ with E, we take an effective width Δ around E such that Δ is very small in comparision of range over which energy E may very. The range can be specified by the limit $E - \Delta/2$ to $E + \frac{\Delta}{2}$ where $\Delta << E$.

The no. of ministates lying in this range is given by

$$\Gamma(N, V, E; \Delta) \simeq \frac{\partial \Sigma_1(E, V, N)}{\partial E} \cdot \Delta$$

$$\simeq \frac{3N}{2} \frac{\Delta}{E} \Sigma_1(E, V, N)$$

$$\therefore \quad \ln \Gamma(N, V, E; \Delta) \simeq N \ln\left[\frac{V}{h^3}\left(\frac{4\pi m E}{3N}\right)^{3/2}\right] + \frac{3N}{2} + \ln\left(\frac{3N}{2}\right) + \ln\left(\frac{\Delta}{E}\right)$$

$\because \ln\left(\frac{3N}{2}\right) << \frac{3N}{2}$ and $\frac{\Delta}{E} << 1$ for $N >> 1$,

therefore,

$$\ln \Gamma(N, V, E; \Delta) \simeq N \ln\left[\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{3N}{2}$$

It shows that the width Δ does not create much difference to the microstates. Only energy E is creating a difference not the width Δ to the microstates.

Calculation of thermodynamic quantities

entropy of the system of non-interacting distinguishable particles

$$S(N, V, E) = K \ln \Gamma(N, V, E)$$

$$= NK \ln\left[\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{3NK}{2}$$

Energy of the system

$$E(S,V,N) = \left\{\exp\left[\frac{2S}{3NK} - 1\right]\right\} \cdot \left\{\frac{3h^2N}{4\pi m V^{2/3}}\right\}$$

$$= \frac{3h^2N}{4\pi m V^{2/3}} \exp\left(\frac{2S}{3NK} - 1\right)$$

Temperature of the system

$$T = \left(\frac{\partial E}{\partial S}\right)_{N,V}$$

$$= E \cdot \frac{2}{3NK}$$

$$\Rightarrow \quad E = \frac{3}{2} NKT \qquad , \qquad N = nN_A$$

$$E = \frac{3}{2} nRT$$

Specific heat at constant volume C_V

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} = \frac{3}{2} NK = \frac{3}{2} nR$$

Pressure

$$P = \left(\frac{\partial E}{\partial V}\right)_{N,S}$$

$$= \frac{2}{3}\frac{E}{V}$$

$$PV = \frac{2}{3}E = nRT$$

specific heat at constant pressure C_p

$$C_p = \left(\frac{\partial H}{\partial T}\right)_{P,N} = \left[\frac{\partial(E+PV)}{\partial T}\right]_{P,N}$$

$$= \frac{5}{2}nR$$

$$\therefore \quad \gamma = \frac{C_p}{C_v} = \frac{5}{3}$$

References:

- Statistical Mechanics by R. K. Pathria
- Statistical Mechanics by B. K. Agarwal and M. Eisner
- An Introductory Course of Statistical Mechanics by P. B. Pal

Thank You

For any questions/doubts/suggestions and submission of assignments

Write at E-mail: akgupta@mgcub.ac.in