Elementary Statistical Mechanics

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Content

In this lecture following topics will be discussed in detail:

- Ensembles,
- Partition function,
- M-B distribution Law

Ensembles : introduced by Gibbs

- Ensemble is defined as a collection of large number of macroscopically identical (same P, V, T, N) but essentially independent systems.

1. Macrocanonical ensemble : collection of essentially independent systems having same energy E, Volume V & number of particles N.
2. Canonical ensemble : collection of essentially independent systems having same temperature T, Volume V & number of particles N.
3. Grand canonical ensemble : collection of essentially independent systems having same temperature T, Volume V & chemical potential μ.

Partition function or sum of states

- Boltzmann's canonical distribution Law gives number of molecules in each cell as a function of energy associated with each particle in that cell. $n_i = Ae^{-\beta E_i}$ A is constant, $\beta = 1/KT$
- Consider zone of cells (having number of cells g_i) then number of molecules in the zone

$$n_i = Ag_ie^{-\beta E_i} \text{ then}$$

- $N = \sum n_i = A\sum e^{-\beta E_i} = ZA$ where Z is partition function.
- Hence $n_i = Ne^{-\beta E_i}/Z$
- Entropy of a monoatomic gas is related with Z :
- $S = R[\log Z + (3/2)]$

Maxwell-Boltzmann Law

- M-B statistics is applied on closed systems in which total number of particles (N) and total energy (E) of system is fixed. n is particles in each cell. $N=\sum n_i$ = constant and $E= \sum n_i E_i$= constant
- Particles are identical and distinguishable.
- There is no restriction on number of particles having same specific energy.
- The equilibrium state of a system is the state of maximum probability.

Distribution law of velocities

- Boltzmann's canonical distribution Law gives number of molecules in each cell as a function of energy associated with each particle in that cell.

$$n_i = Ae^{-\beta E_i} \qquad \text{A is constant, } \beta = 1/KT$$

Using position coordinates and velocity coordinates, further it gives the number of molecules having x component of velocity in the range between v_x and v_x+dv_x

$$n(v_x)dv_x = N(m/2\pi KT)^{1/2}\, e^{-mv_x^{2}/2KT}\, dv_x$$

Probability that a molecule will have x-component of velocity in the range between v_x and v_x+dv_x is given by

$$P(v_x)dv_x = n(v_x)dv_x /N = (m/2\pi KT)^{1/2}\, e^{-mv_x^{2}/2KT}\, dv_x$$

above both equations represents Maxwell's distribution Law of velocities.

Most probable velocity $v_x = (2KT/m)^{1/2}$

Zartman and C.C. Ko Experiment is an accurate test of Maxwell's law of distribution of velocities.

Limitations of Maxwell- Boltzmann's Method

- Applicable only on isolated gas which is said to be ideal and non-degenerate.
- Correct expression for Entropy (S) of ideal gas is obtained by resolving Gibbs paradox.
- The expression for S does not satisfies the third law of thermodynamics.
- It can not be applied to a system of indistinguishable particles.
- Not valid at very low temperature and at very high particle density.
- It fails to explain specific heat at low temperature, photoelectric effect, black body radiation.

Reference book:
Heat thermodynamics and statistical physics by Brijlal et all.

Please try to solve:

1. What is Gibbs Paradox?

2. In grand canonical ensemble remains same:

   1)T,V,N 2) T, V, μ 3) E,V,N 4) P,V,T

3. What is Equation for Partition function in microcanonical and grand canonical ensemble?

4. What is Equation for entropy of ideal gas?

5. Explain temperature and velocity curve on the basis of Maxwell distribution law of velocities.

6 What is most probable velocity?

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