

Statistical mechanics

Paper:-GE2T

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References :

1. Thermal physics by A.B Gupta& H. Roy
2. Lecture note by S.Swasmal

Phase space : In classical mechanics, the instantaneous dynamical state of a particle is completely specified by its three position co-ordinates (x, y, z) and three corresponding momentum co-ordinates (p_x, p_y, p_z) . Thus six co-ordinates are needed to specify a "one particle system" completely. These six co-ordinates (x, y, z, p_x, p_y, p_z) are marked along six mutually perpendicular axes in six-dimensional space. This six dimensional space is called "phase space".

↳ Phase point : The point in phase space representing the instantaneous state of the particle is called phase point.

↳ Phase density : The number of phase points per unit volume of phase space is called phase density.

↳ Phase cells : When a phase space (or position-momentum space) is divided into tiny six dimensional cells whose sides are $\partial x, \partial p_x, \partial y, \partial p_y, \partial z, \partial p_z$, then such tiny cells are called "phase cells".

↳ Microstate of a system : <V.U - 1998, 2001, 2002, 2006, 2007, 2008>

A system of atomic dimension or smaller size is called microscopic system.

If the state of a system of particles are specified by quoting the position and momentum of individual particles then it is called microstate or microscopic state of the system.



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Example : a molecule, an atom, an ion.

① Macrostate of a system : <V.O - 1998, 2001, 2002, 2006, 2007, 2008>

A system which is large enough to be observable in the ordinary sense, is called macroscopic system.

The macroscopic state or macrostate of a system can be specified by quoting the macroscopic parameters as like pressure, volume, temperature, energy, chemical potential.

Example : Solid, liquid, gas.

② Illustration of microstates and macrostate of a system :

Let us consider a system of three molecules a, b, c which are distributed in two half halves of a box ; left half - L and right half - R.

The distribution of molecules are shown as -

L	R	Distributions.	Microstates	Macrostate
a b c	-	3, 0	1	1
-	a b c	0, 3	1	1
a b	c	2, 1	3	1
b c	a	2, 1		
c a	b	2, 1		
a	b c	1, 2	3	1
b	c a	1, 2		
c	a b	1, 2		

Hence there are four possible distributions -


- 3 molecules in L and 0 molecule in R i.e (3, 0)
- 0 molecule in L and 3 molecules in R i.e (0, 3)
- 2 molecules in L and 1 molecule in R i.e (2, 1)
- 1 molecule in L and 2 molecules in R i.e (1, 2)



Total number of ways in which three molecules can occupy two halves of the box = $1+1+3+3 = 8 = 2^3$ corresponding to four different distributions.

Each way of arrangement of molecules is a microstate of the system while each different distribution of molecules is a macrostate.


Thus there are 8 microstates and 4 macrostates in the above example.

 Accessible state: The microstates which are permitted under the constraints imposed upon the system are called "accessible states".

If there are n_1 molecules in cell 1; each having energy ϵ_1 ,
 n_2 molecules in cell 2; each having energy ϵ_2 ,
and so on, then constraints are - $\sum n_i = N$
and $\sum n_i \epsilon_i = E$.

Details: The microstates which are allowed under given restrictions are called accessible microstates.

For example: In case of 3 molecules, a, b, c to be restricted between two halves of a box. If none of them can be outside the box, then (a, b, c), (a, c, b), (b, c, a) are accessible microstates.

 While (a, b), (b, c), (a, c) are etc. are inaccessible microstates.

① Statistical definition of entropy :

(General)

In equilibrium state both the entropy (S) and thermodynamical probability (ω) have their maximum values.

According to thermodynamics, entropy (S) of a system is related with temperature by the relation,

$$\frac{1}{T} = \frac{\partial S}{\partial E} \text{ ----- ①}$$

According to Statistical mechanics,

$$\beta = \frac{1}{kT}$$

$$\Rightarrow \frac{\partial}{\partial E} (\ln \omega) = \frac{1}{kT}$$

$$\Rightarrow \frac{1}{T} = k \frac{\partial}{\partial E} (\ln \omega) \text{ ----- ②}$$

From equation ① and ②, we may write,

$$\frac{\partial S}{\partial E} = k \frac{\partial}{\partial E} (\ln \omega)$$

$$\Rightarrow \boxed{S = k \ln \omega}$$

Which is the statistical definition of entropy.

② Statistical definition of pressure :

Elementary work done $dW = \frac{1}{\beta} \frac{\partial}{\partial V} (\ln Z) dV$.

$$\Rightarrow p dV = \frac{1}{\beta} \frac{\partial}{\partial V} (\ln Z) dV$$

$$\Rightarrow p = \frac{1}{\beta} \frac{\partial}{\partial V} (\ln Z)$$

$$\Rightarrow \boxed{p = kT \frac{\partial}{\partial V} (\ln Z)}$$

Where Z is the partition fn.

① Statistical definition of chemical potential :

$$dE = Tds - pdv + \sum_i F_i d\lambda_i$$

where $F_i = \left(\frac{\partial E}{\partial \lambda_i}\right)_{s,v}$ is called the generalised force .

$$\Rightarrow dE = Tds - pdv + \mu dN$$

$$\Rightarrow \boxed{\mu = \left(\frac{\partial E}{\partial N}\right)_{s,v}}$$

called ~~thermo~~ statistical chemical potential

② Third law of thermodynamics : (v.u - 2001, 2008)

" Every system has a finite positive entropy, but at absolute zero temperature the entropy may become zero "



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NEXT CLASS:

- Quantum statistics