

M. N. SAHA AND R. C. MAJUMDAR

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At the present time a number of new methods are being developed in statistical mechanics, and it is difficult to see the connexion amongst them. In this essay an attempt is made to review these methods and supply the link amongst the different theories.

Almost all the old (Planck) and new methods (Bose-Einstein⁽¹⁾, Fermi-Dirac⁽²⁾) start with Boltzmann's theorem

$$S = k \log W,$$

and with Planck's definition of W , viz.:-

W = Thermodynamical Probability.

There is an alternative function G due to Boltzmann⁽³⁾ and Gibbs⁽⁴⁾ which may be described as the total phase volume described by a thermodynamical system. Ehrenfest and Trkal⁽⁵⁾ treat problems of chemical equilibrium etc. with the aid of this function (they called it $\{\gamma\}$), and find their method superior to Planck's. There is a certain amount of ambiguity in Planck's definition of W ; according to him W is a whole number, but Ehrenfest and Trkal have shown that Planck's expression for W has to be divided by $N!$ to get the correct expression for S . The need for this operation is not clear. Planck⁽⁶⁾ has apparently admitted the soundness of this criticism, and in a recent paper puts a new interpretation on W . He defines W as the maximum number of probable states which can give rise to the total energy E . Planck shows that, with this definition,

$$W = \frac{G}{h^{3N} N!} \quad (1)$$

The same conclusion has been reached independently and simultaneously by Saha and Sur⁽⁷⁾ from different conceptions. They emphasize the necessity for laying down a unit of probability. At absolute zero $S=0$ and $W=1$, and the total phase-volume described = $h^{3N} N!$ in the simplest case (i.e., a perfect monatomic gas). Denoting this by G_0 , and the corresponding probability by unity, the mathematical value of probability at any temperature

$$W = \frac{G}{G_0} = \frac{G}{h^{3N} N!}.$$

The conceptions of Planck and Saha and Sur, though apparently different, are in essence identical.

We shall therefore start with the theorem (1) and calculate W , introducing (1) classical conceptions, (2) the Fermi-Dirac condition, (3) the Bose-Einstein condition.

Let us suppose the assembly to be distributed in equi-energy layers with the energy-interval $(\epsilon_s, \epsilon_s + d\epsilon_s)$ for each particle, and let N_s be the number of particles in this interval. The phase-volume occupied by each particle

$$g_s = 2\pi V (2m)^{3/2} \epsilon_s^{1/2} d\epsilon_s. \quad (2)$$

Then, according to Ehrenfest and Trkal,

$$G = \frac{N!}{\prod_s N_s!} \prod_s g_s^{N_s} \quad (3)$$

This theorem has been given by Ehrenfest and Trkal without proof, though to many it may not be so self-evident. We are therefore supplying a proof. Let G_N denote the phase-space described by N -particles, and G_{N-1} the phase-space described by $N-1$ -particles, the remaining particle being assigned to the region $(dx dy dz dp_x dp_y dp_z)$. We have

$$G_N = \frac{V^N (2\pi m)^{3N} E^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2} + 1\right)} \quad (3')$$

Now we have⁽⁸⁾

$$\frac{G_{N-1}}{G_N} = \frac{dw}{d\tau} \quad (4)$$

where dw is the probability that the particle is to be found in the phase-volume considered. We have therefore

$$dw = \frac{N_s}{N},$$

and $d\tau$ the phase-volume of the particle under question = g_s . Thus

$$G_N = G_{N-1} \cdot \frac{g_s}{(N_s/N)}$$

Then by successive application of the same theorem

$$G_N = G_{N-n} \left(N \frac{g_s}{N_s} \right)^{n_s},$$

and finally, taking all the energy-layers,

$$G_N = \prod_s g_s^{N_s} \left(\frac{N}{N_s} \right)^{N_s} = \frac{N!}{\prod_s N_s!} \prod_s g_s^{N_s} \quad (3)$$

We have thus reduced the calculation of the phase-volume from the $6N$ dimensional space to one of 6

* Communicated by the Authors.

dimensions. We shall now show that the classical expression for entropy is easily obtained from this value of G. We have

$$W = \frac{1}{\prod N_s!} \prod_s \left(\frac{g_s}{h^3} \right)^{N_s}$$

Let $\frac{g_s}{h^3}$ be denoted by a_s ;

then $S = k \log W$

$$= k \left\{ \sum_s N_s \log a_s - \sum_s N_s (\log N_s - 1) \right\}$$

$$= k \sum_s N_s \log \frac{a_s}{N_s} + KN. \quad (4)$$

Now $E = \sum_s N_s \epsilon_s$

$$N = \sum_s N_s \quad (5)$$

Hence, applying the variation-principle,

$$\left. \begin{aligned} \delta S &= \sum_s \delta N_s (\log a_s - \log N_s) \\ \delta N &= \sum_s \delta N_s \\ \delta E &= \sum_s \delta N_s \epsilon_s \end{aligned} \right\} \quad (6)$$

Therefore $\log a - \log N + \lambda \epsilon_s + \mu = 0$

or $N_s = \alpha a_s e^{\beta \epsilon_s}$ (7)

It can now be easily proved in the usual way that

$$\beta = -\frac{1}{kT}, \text{ and } \frac{1}{\alpha} = \frac{V}{Nh^3} (2\pi mkT)^{3/2} \quad (8)$$

and substituting these values, we can easily show that S gets the classical value, viz.,

$$Nk \log \left\{ \frac{V}{Nh^3} (2\pi mkT)^{3/2} e^{5/2} \right\} \quad (9)$$

Now we shall show how the Fermi-Dirac expression can be obtained from the definition of W.

The phase-volume of the assembly

$$G = \frac{N!}{\prod N_s!} \prod_s g_s^{N_s}$$

has been calculated on the supposition that the phase-volume occupied by each individual particle is infinitely small compared with the total phase-volume at its disposal, viz., g_s . Let us now give up this assumption, and suppose it occupies a finite phase-volume "a". Then

$$G = \frac{N!}{\prod N_s!} \prod_s g_s (g_s - a) \dots (g_s - \overline{N_s - 1}a). \quad (10)$$

The argument is just the same as that which we introduce in the calculation of the van der Waals's correction "b" from probability consideration. When each particle occupies negligible volume we have

$$W \propto V^N;$$

but when the volume "β" cannot be neglected,

$$W \propto \prod_{\gamma=1}^N (V - \overline{\gamma - 1} \beta).$$

In the above method we have introduced the phase-volume g_s instead of the space-volume V, and calculated G_N . Now

$$W = \frac{G}{h^{3N} N!}$$

$$= \frac{1}{\prod N_s!} \prod_s \left(\frac{g_s}{h^3} \right) \dots \left(\frac{g_s}{h^3} - \overline{N_s - 1}a \right)$$

$$= \frac{1}{\prod N_s!} \prod_s a_s (a_s - \epsilon) \dots (a_s - \epsilon \cdot \overline{N_s - 1}),$$

where $\epsilon = \frac{a}{h^3}$

$$= \frac{a_s!}{s N_s! (a_s - \epsilon N_s)!} \quad (11)$$

If we put $\epsilon = 1$, we get the Fermi-Dirac expression for W; when $\epsilon = -1$ we have

$$W = \frac{\prod_s a_s + \overline{N_s - 1}!}{s (a_s - 1)! N_s!} \quad (12)$$

which is the Bose-Einstein expression for W.

It may be mentioned here that the above discussion was originally inspired by an article of L. Brillouin (*Ann. d. Phys.* vii. 1927). But in spite of apparent resemblance, the method given here differs in essential points from Brillouin's. Firstly, Brillouin follows Bose-Einstein and Fermi-Dirac closely in calculating probability by making use of a_s (which is Brillouin's g_s) as the number of degrees of freedom which a particle can have when its energy lies between ϵ_s and $\epsilon_s + d\epsilon_s$. It may be easily shown that though we obtain the various values of N_s by subjecting Brillouin's expressions for W to the usual variational process in the three different cases (equations 21), they do not give us absolute values of entropy unless some assumption is made regarding the value of A or G in equation (21) of Brillouin. We have to make $\frac{G}{a} = N$ in order to get the correct value of S. The justification

for this assumption is not clear, and Brillouin has made no attempt to calculate the absolute value of S. He devotes a good deal of discussion over the origin of the permutability factors $\frac{N!}{\prod N_s!}$, which is quite unnecessary. The factor comes out automatically when we calculate the total phase-volume of the ensemble not in 6N dimensions, but in 6 dimensions.

The above method has therefore the merit of giving a deduction for the absolute value of S on the three views from a unitary standpoint. The classical statistics and Fermi-statistics are easily understandable, and probably in the case of Fermi-Dirac statistics it affords a clearer physical view of the case than Fermi's original method. There may be many who share with us the difficulty in understanding

the extension of the Pauli Principle, which has been shown to be the guiding principle in the formation of atoms out of protons and electrons, to the case of an ensemble of N independent particles possessing only translatory motion (e. g., Hall, Proc. Nat. Acad. Sci. 1928). The deduction given here follows exactly the same lines as the deduction of the van der Waals's correction for finite volumes, and is therefore physically more comprehensible.

Of greater difficulty is the comprehension of the Bose-Einstein statistics. Here " ω ", the phase-volume of any particle, has to be put negative ($-h^3$). These statistics have therefore to be definitely ruled out in the case of material particles. But as it is found to be correct in the statistics of light-particles, we have to assume that when a photon enters a phase-space, the space expands, since the total

phase-volume is increased by the phase-volume of the photon. A discussion will be found in Brillouin's paper above referred to.

References

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- (2) Fermi, *Zeits. f. phys.* xxxvi. p. 902 (1926). Dirac, *Proc. Roy. Soc. A*, cxii. p. 66, (1926).
- (3) Boltzmann, "Über die Eigenschaften Monozyklischer System" *Wien. Ber.* xc. (1884); *Wiss. Abhandl.* iji. Nr. 73, S. 132ff.
- (4) Gibbs, 'Statistical Mechanics.'
- (5) Ehrenfest and Trkal, *Proc. Amst. Acad.* xxiii. (1920).
- (6) Planck, *Zeits. f. phys.* xxxv. p. 155 (1925).
- (7) Saha and Sur, *Phil. Mag.* i. p. 280 (1926).
- (8) Jeans, 'Dynamical Theory of Gases,' 2nd ed. chap. iv. pp. 58-62. Wassmuth, *Statistische Mechanik.*

48. COLOURS OF INORGANIC SALT

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No satisfactory explanation of the colours of inorganic salts in the vapour state, in solution, or in crystalline form has yet been put forward, excepting certain suggestions by Fajans ("Handbuch der Physik", Bd. 24, p. 564), that the colours are due to the deformation of the cation produced by surrounding anions and molecular complexes. The ideas of Fajans were rather vague, but the time has now come to put forward a more precise hypothesis. It is well known that salts like NaCl, CaCl₂, AlCl₃ in which the electrons of the cation form closed shells (p^6), are colourless or white. Herzfeld found from a study of dispersion of NaCl that there are three ultra-violet absorption bands, one at $\lambda 340$ which was ascribed to Na⁺, another at about $\lambda 1500$, which was ascribed to Cl⁻-ion. This last one has been experimentally obtained by Pfund (*Phys. Rev.*, vol. 32) by the *Reststrahlen* method. The wave-length $\lambda 340$ ascribed to Na⁺ agrees remarkably well with the resonance line of Na⁺ identified by K. Majumdar (*Ind. Jour. Phys.*, 1927) and Bowen, though definite assignment of values of the absorption wave-length from dispersion data in this region is subject to certain uncertainties.

Colours are almost entirely shown by the compounds of the transitional group of elements (the first group consisting of elements from scandium to copper). Let us fix our attention on the first group alone, as the same arguments will apply to other groups. The colours are somewhat modified by the anion, or the state of aggregation (solution or crystal), but intrinsically it is due to the cation. Taking a compound like CrCl₃, we can say that it consists of a Cr⁺⁺⁺-ion, surrounded by three Cl⁻-ions. The absorption of light in the visible region is due entirely to the outer

electrons of the Cr⁺⁺⁺-ion. Let us see how this absorption takes place.

The outermost shell of the Cr⁺⁺⁺-ion (and generally of all ions of transitional elements) consists of a number of electrons in the d -shell. In Cr⁺⁺⁺, the number is 3. The multiplicity of the most stable combination state is obtained by adding up the multiplicity vector $r = \frac{1}{2}$ for all the electrons, and the next metastable states are obtained by reversing the vector r for one of the electrons. In d^3 , the states are respectively 4X and 2Y , where X and Y are further to be formulated. This is obtained by considering the l -coupling according to Pauli's principle, and in the case of Cr⁺⁺⁺, $X = F$ and P in 4X , and $Y = H, G, D$ in 2Y . The average difference in energy between the terms obtained in this way, that is, by having the rotating quantum number all in one direction, and then reversing only one, is about $C_{av} = 20,000$, the value increasing with the number of net charges in the nucleus, as shown by the spectroscopic data of Russell, Gibbs and White, Lang, Shenstone, etc. (see various papers in the *Physical Review*).

It is therefore evident that the absorption of light in the visible region is due to some of the κ -electrons changing their r -vector from $\frac{1}{2}$ to $-\frac{1}{2}$. This type of transition is possible only in transitional groups, and though usually forbidden they become very prominent in all molecular formations. We cannot, of course, expect that the values of energy difference which we obtain from spectroscopic studies will continue to hold good in molecules or complex formation, but they will remain of the same order of magnitude. An indefiniteness will be introduced by the modification of the rules of l -coupling (*vide* Stoner's