

# AN ESSENTIALLY STATISTICAL APPROACH TO THE THERMODYNAMIC PROBLEM

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## I. INTRODUCTION.

Though it is generally admitted that the methods of mechanics are not suitable for solving thermodynamic problems, yet the mechanical bias predominates in all the existing methods of statistical thermodynamics. In statistical thermodynamics, the problems, as usually formulated are essentially of mechanical nature and the probabilistic or statistical arguments are generally introduced as substitutes of mechanical methods, if and only when they fail. Now, in microscopic approaches to the thermodynamic problems, the thermodynamic systems are usually assumed to be composed of large numbers of constituent parts, of which the nature is not really known but is only postulated conveniently as mechanical. So an essentially statistical method, free from mechanical hypotheses about the nature of constituent parts, for the interpretations of thermodynamic problems may be considered desirable and overdue. Even, discussions of the classical phenomenological thermodynamics, according to which in a thermodynamic (equilibrium) state any physical quantity signifying some behaviour of the system can have only one value, when modified in light of the notions of fluctuations in the values of physical quantities based on the experiments on light-scattering, on the torsional oscillations of mirror suspended in high vacuum, etc., necessitates a purely statistical approach to these problems. In this paper, an attempt has been made to pursue an essentially statistical method for treatment of such problems.

With this end in view, a mathematical probability of occurrence of the system under consideration, in any state (which will be defined in the next section), has been suitably introduced in this paper as the starting point of the discussion. As defined, the expression for the probability contains two distribution-parameters, which, by introduction of suitable assumption analogous to the principle of maximum likelihood, are determined and are correlated with the 'real' state (observed in the sense of classical phenomenological thermodynamics<sup>1</sup>). Up to this, all discussions have been made for the system kept in a definite environment. In the later portion of this paper, the environment of the system under consideration is slightly varied and the effects of the variations on the average behaviour of the system are calculated by introduction of the equation of continuity in a suitable form. Some important functions, characterising the behaviour of the equation of continuity, are identified as the entropy, the temperature and the chemical potential of the system. Other important results, viz., the non-decreasing property of entropy, statistics for microscopic distribution and the formulae for fluctuations, have been subsequently investigated.

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<sup>1</sup> In future, 'in the sense of classical phenomenological thermodynamics' will be shortly referred to as 'in the classical sense'.

## II. FORMULATION OF THE PROBLEM.

In this paper, the system means some finite quantities,  $M$  and  $E$ , of two types of entities, viz., matter and energy, enclosed in a definite volume in a definite environment.<sup>1</sup> In the discussion, if not specifically mentioned, the system is to be taken as open, i.e., there is no hindrance on free transfer of matter and energy between the system and the environment. The state of the system in a definite environment is taken as specified when a set of values  $(M, E)$  is ascribed to the quantities of matter and energy contained in the system. In contrast to the term 'real', used in the previous section, all these states will be referred to as 'virtual' states. In this connection it should be noted that the 'virtual' states are not purely hypothetical and not devoid of physical significance. They are realisable and are significant in experiments connected with fluctuation-phenomena; or better, they (the virtual states) are the fluctuating states about the real (thermodynamic) state.

The basic statistical investigation of this paper really consists of two simpler problems. The first is how to determine the law of distribution of occurrences of the system in a definite environment amongst states, from the knowledge of observed values of  $M$  and  $E$  in real states by introducing plausible assumptions. The other is how to investigate the consequences of changes in the environment of the system. From these all the usual informations of microscopic distribution are also obtained by introducing suitable assumptions about the constituent parts.

For simplicity, at present, the system will be assumed to be composed of chemically single type of material, and  $M$  and  $E$  are assumed to have discrete values. This is also quite in agreement with other modern methods according to which the system, being essentially a quantum system and being composed of molecules or the like, generally assumes discrete set of values of  $M$  and  $E$ .

## III. THE LAW OF PROBABILITY-DISTRIBUTION.

Due to perfect randomness in values of  $M$  and  $E$  in virtual states of systems, corresponding to the same and the different environments, the matter and the energy contained in the system will be taken as unrelated entities. So it will be assumed that in a definite environment there is a constant *a priori* probability  $t$  for each unit quantity of matter to occur in the system considered, and that there is a constant *a priori* probability  $z$  for each unit of energy, such that for a quantity of matter of mass  $m$  it will be  $t^m$ , and for quantity of energy  $e$  it will be  $z^e$ .

Thus, if  $W(E, M)$  be the weight of the states, i.e., the number of ways in which  $(E, M)$  can be realised together in the system, then the probability of occurrences of the system in the state specified by  $(M, E)$  is

$$P(t, z; E, M) = \frac{W(E, M) \cdot t^M \cdot z^E}{\sum_{E=0}^{\infty} \sum_{M=0}^{\infty} W(E, M) \cdot t^M \cdot z^E} = \frac{W(E, M) \cdot t^M \cdot z^E}{f(t, z)}, \quad \dots \quad (1)$$

where

$$f(t, z) = \sum_{E=0}^{\infty} \sum_{M=0}^{\infty} W(E, M) \cdot t^M \cdot z^E. \quad \dots \quad (2)$$

The function  $f(t, z)$  is the usual characteristic function.

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<sup>1</sup> In future, 'enclosed in a definite volume in a definite environment' will be simply referred to as 'in the definite environment'.

In the present discussion, for specification of distribution-law,  $P(t, z; E, M)$  will be considered as functions of  $t, z$  and  $E, M$  will be considered as parameters, and so this will be briefly written as  $P(t, z)$ .

The expression (1) can also be written from a slightly different consideration. Now, if an equal *a priori* probability  $p$  be associated with all possible environments, and if one of the environments has the productive probabilities  $t$  and  $z$  respectively for unit quantity of matter and energy to occur in the system, and if  $W(E, M)$  is used with the same significance as in the above, then the probability of occurrence of  $M$  and  $E$  is also given by (1).

In the expression (1) for  $P(t, z)$  the possibility of infinite variation of  $M$  and  $E$  has been admitted. This will remind one of the infinite heat-bath (of course, here, infinite heat- and matter-bath) in the usual discussions of canonical assembly. But, even when the upper limit of variations of  $M, E$  be restricted to some large number  $\mathcal{N}$  and  $\mathcal{E}$  (as the case should always be in consequence of relativistic concept of finite universe), the expression for probability can also be put in the form (1). Let  $t'^M$  and  $z'^E$  be as before *a priori* probabilities of  $M$  and  $E$  to occur in the system and then as the universe is finite, so  $(1-t')^{\mathcal{N}-M}$  and  $(1-z')^{\mathcal{E}-E}$  should be taken as *a priori* probability of  $\mathcal{N}-M$  and  $\mathcal{E}-E$  occurring outside the system. Thus, with usual significance for  $W(E, M)$ , the probability can be written as

$$\begin{aligned} P(t', z'; E, M) &= \frac{W(E, M) \cdot t'^M \cdot z'^E \cdot (1-t')^{\mathcal{N}-M} \cdot (1-z')^{\mathcal{E}-E}}{\sum_{M=0}^{\mathcal{N}} \sum_{E=0}^{\mathcal{E}} W(E, M) \cdot t'^M \cdot z'^E \cdot (1-t')^{\mathcal{N}-M} \cdot (1-z')^{\mathcal{E}-E}} \\ &= \frac{W(E, M) \cdot \left(\frac{t'}{1-t'}\right)^M \cdot \left(\frac{z'}{1-z'}\right)^E}{\sum_{E=0}^{\mathcal{E}} \sum_{M=0}^{\mathcal{N}} W(E, M) \cdot \left(\frac{t'}{1-t'}\right)^M \cdot \left(\frac{z'}{1-z'}\right)^E} \\ &= \frac{W(E, M) \cdot t^M \cdot z^E}{\sum_{E=0}^{\mathcal{E}} \sum_{M=0}^{\mathcal{N}} W(E, M) \cdot t^M \cdot z^E} \\ &= P(t, z), \end{aligned}$$

where  $t = \frac{t'}{1-t'}$  and  $z = \frac{z'}{1-z'}$ .

This is of the same form as (1), only interpretations and ranges of  $t$  and  $z$  are different. The summation can also be extended to infinity as due to finiteness of total energy and matter in the universe,

$$W(E, M) = 0, \text{ when } M > \mathcal{N} \text{ or } E > \mathcal{E}.$$

For determination of the distribution-parameters  $t$  and  $z$ , in agreement with usual idea of statistical equilibrium, it will be assumed that the 'real' values  $M_0$  and  $E_0$  (taken to be known from observations in the classical sense) correspond to the maximum of probability of occurrence, considered as function of  $t$  and  $z$ . This assumption is quite similar to the principle of maximum likelihood. Again the present idea of associating a probability-distribution of  $(M, E)$ , besides a set of  $(M_0, E_0)$ , to each 'real' state is also similar to that of Szilard (1925).

IV. BEHAVIOUR OF THE FUNCTIONS  $W(E, M)$ ,  $f(t, z)$ ,  $P(t, z)$ .

It is now necessary to discuss the nature of  $W(E, M)$  and of the series in the denominator of the relation (1) denoted by  $f(t, z)$ . This discussion will help to form ideas about the nature of the probability function  $P(t, z)$ , and to show that the function  $P(t, z)$  has really a unique maximum.

For the clear understanding of the above, in the beginning, some well-known special cases are discussed, and then, as a way of generalisation necessary postulates about the nature of the above functions have been introduced for general cases. With this end in view, the case of the system in gaseous phase (where contributions of the radiation-energy and the mutual-interaction-energy are not significant) has been discussed in details. Let us denote  $\frac{M}{m}$  by  $N$ , where  $m$  is the mass of each constituent part of the system. In this case,  $W(E, M)$  is partition of the number  $E$  into  $N$  parts according to certain rule of partition and so is essentially a positive integer, and as a way of definition,  $W(0, 0)$  is to be taken as one. Obviously  $W(E, M)$ , being partitions of a number  $E$  into  $N$  parts, depends on the instantaneous numerical values of  $E$  and  $N$  and is to be taken as independent of all external parameters. In the general case, as a way of generalisation, it will be taken that  $W(E, M)$  is essentially a positive integer and is independent of external parameters.

To have the clear insight about the behaviour of  $f(t, z)$  as in the above, simple cases will be discussed first. In the simplest case, the energy-levels for constituent parts may be taken as equidistant and non-degenerate, i.e.  $E_i = i\Delta$ , such that energy-quanta are simple integral multiple of same quantum of energy. Here, if  $\Delta$  is taken to be unit of measurement for energy, then the set of values of  $E$  will be set of integers. In these cases, discussions proceed very simply as follows.

*Case A:*

The system is such that any number of constituent parts may have the same energy. This corresponds to the case of ensembles of Bose-Einstein particles. Here  $W(E, M)$  is the partition of energy  $E$  into  $N$  parts with no restriction.

Then,

$$W(E, M) = P(E/N/*), \quad \dagger \quad \dots \quad (3)$$

and

$$f(t, z) = \prod_{n=0}^{\infty} (1 - t^n \cdot z^n)^{-1}. \quad \dots \quad (4)$$

*Case B:*

The system is such that no two constituent particles can have simultaneously equal energies. This case corresponds to the case of ensemble of Fermi-Dirac particles. Here  $W(E, M)$  is partition of  $E$  into  $N$  parts where no two parts can be equal. Then,

$$W(E, M) = P_{(\neq 1)}(E/N/*), \quad \dots \quad (5)$$

and

$$f(t, z) = \prod_{n=0}^{\infty} (1 + t^n z^n). \quad \dots \quad (6)$$

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† Notations, used here for partition of numbers, are similar to those in *Algebra* (Part II), G. Chrystal. (1922, A. and C. Black Ltd., London.)

Case C:

The system under consideration is such that the number of constituent parts, having simultaneously equal energies, cannot exceed a certain fixed number  $d$ . This corresponds to Gentile's statistics. In this,  $W(E, M)$  is the partition of  $E$  into  $N$  parts in which up to  $d$  repetitions are possible. Then,

$$W(E, M) = P_{(\nearrow d)}(E/N/\bar{*}), \quad \dots \quad (7)$$

and

$$f(t, z) = \prod_{n=0}^{\infty} \left\{ \frac{1 - t^{m(d+1)} \cdot z^{n(d+1)}}{1 - t^m \cdot z^n} \right\}. \quad \dots \quad (8)$$

Case D:

In the case, when the constituent parts are localised and distinguishable, these become

$$W(E, M) = \frac{(E+N-1)!}{N! (N-1)! E!}, \quad \dots \quad (9)$$

and

$$\begin{aligned} f(t, z) &= \sum_{N=0}^{\infty} \sum_{E=0}^{\infty} \frac{1}{N!} \cdot \frac{(E+N-1)!}{(N-1)! E!} \cdot t^{mN} \cdot z^E \\ &= \sum_{N=0}^{\infty} \frac{1}{N!} \cdot t^{mN} \cdot (1-z)^{-N} = e^{\frac{t^m}{1-z}} \\ &= e^{t^m \cdot \sum_0^{\infty} z^n} \\ &= \prod_{n=0}^{\infty} e^{t^m \cdot z^n}. \end{aligned}$$

The above discussion can be very easily extended to the case where there is a degeneracy of eigen-states in energy levels, i.e. where every energy-level is not of equal weight as in the case of degeneracy. If  $A_n$  be the weight of  $n$ th energy-level (i.e. the degree of degeneracy of states), then the above formulae can be written as follows:

Case A:

$$f(t, z) = \prod_{n=0}^{\infty} (1 - t^m \cdot z^n)^{-A_n}. \quad \dots \quad (4')$$

Case B:

$$f(t, z) = \prod_{n=0}^{\infty} (1 + t^m \cdot z^n)^{A_n}. \quad \dots \quad (6')$$

Case C:

$$f(t, z) = \prod_{n=0}^{\infty} \left\{ \frac{1 - t^{m(d+1)} \cdot z^{n(d+1)}}{1 - t^m \cdot z^n} \right\}^{A_n}. \quad \dots \quad (8')$$

Case D:

$$f(t, z) = \prod_{n=0}^{\infty} e^{A_n \cdot t^m \cdot z^n}. \quad \dots \quad (10')$$

The present discussion can also be very simply extended to the cases where the energy-levels are not equally spaced and the corresponding expression can be obtained as follows:

Case A:

$$f(t, z) = \prod_{n=0}^{\infty} (1 - t^m \cdot z^{\epsilon_n})^{-1}, \quad \dots \dots \dots (11)$$

and in the case of degeneracy,

$$f(t, z) = \prod_{n=0}^{\infty} (1 - t^m \cdot z^{\epsilon_n})^{-A_n}, \quad \dots \dots \dots (12)$$

Case B:

$$f(t, z) = \prod_{n=0}^{\infty} (1 + t^m \cdot z^{\epsilon_n}), \quad \dots \dots \dots (13)$$

and in the case of degeneracy,

$$f(t, z) = \prod_{n=0}^{\infty} (1 + t^m \cdot z^{\epsilon_n})^{A_n}, \quad \dots \dots \dots (14)$$

Case C:

$$f(t, z) = \prod_{n=0}^{\infty} \left\{ \frac{1 - t^{m(d+1)} \cdot z^{(d+1)\epsilon_n}}{1 - t^m \cdot z^{\epsilon_n}} \right\} \dots \dots (15)$$

and in the case of degeneracy,

$$f(t, z) = \prod_{n=0}^{\infty} \left\{ \frac{1 - t^{m(d+1)} \cdot z^{(d+1)\epsilon_n}}{1 - t^m \cdot z^{\epsilon_n}} \right\}^{A_n}, \quad \dots \dots (16)$$

where  $\epsilon_n$  is the energy of the  $n$ th energy-state of the constituent parts, and  $A_n$  is the degree of degeneracy of  $n$ th energy-state.

Now, as in the cases discussed here,  $f(t, z)$  has been found to be expressible in form of infinite product, and as  $t$  and  $z$  lie between 0 and 1, so the continuity, the differentiability, etc. of  $f(t, z)$  follow simply from the well-known properties of infinite product. When  $\epsilon_n$ 's are commensurable, such that ultimately they are expressible as integers with a suitable choice of the unit of energy, then  $f(t, z)$  also reduces to the form referred above. For other case, i.e. when  $\epsilon_n$ 's are not commensurable, careful analysis is required and is postponed at present for future. Here, in general,  $f(t, z)$  and so  $P(t, z)$  will be postulated as a function of  $t$  and  $z$  having continuous derivatives of first two orders within the domain of  $t$  and  $z$ .

*Theorem:* If  $f(z)$  be the characteristic function of the system and if it is possible to distinguish in it two groups which together make up the whole system and have characteristic function  $f_1(z)$  and  $f_2(z)$  respectively, then the characteristic function of the entire system is factorisable as  $f(z) = f_1(z) \cdot f_2(z)$ .

Let  $M_1, M_2$  be the number of particles in two groups, where  $M_1 + M_2 = M$  and let  $E_1$  and  $E_2$  be corresponding energies, where  $E_1 + E_2 = E$  at any instant. Then,

$$W(E, M) = \sum_{\substack{E = E_1 + E_2 \\ M = M_1 + M_2}} W_1(E_1, M_1) \cdot W_2(E_2, M_2) \dots \dots \dots (17)$$

$$\therefore f(t, z) = \sum_{M=0}^{\infty} \sum_{E=0}^{\infty} W(E, M) \cdot t^M \cdot z^E$$

$$\begin{aligned} \therefore f(t, z) &= \sum_{M=0}^{\infty} \sum_{E=0}^{\infty} \sum_{\substack{E = E_1 + E_2 \\ M = M_1 + M_2}} W_1(E_1, M_1) \cdot W_2(E_2, M_2) \cdot t^{M_1 + M_2} \cdot z^{E_1 + E_2} \\ &= \left\{ \sum_{M_1=0}^{\infty} \sum_{E_1=0}^{\infty} W_1(E_1, M_1) \cdot t^{M_1} \cdot z^{E_1} \right\} \\ &\quad \times \left\{ \sum_{M_2=0}^{\infty} \sum_{E_2=0}^{\infty} W_2(E_2, M_2) \cdot t^{M_2} \cdot z^{E_2} \right\} \\ &= f_1(t, z) \cdot f_2(t, z) \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (18) \end{aligned}$$

Similarly, it can be shown that if the system may be looked upon as consisting of  $n$  number of sub-systems, then  $f(t, z)$  is factorisable into  $n$  components.

Now, from the equation (1) it is obvious that  $P(t, z) = 0$  when either  $t = 0$ , or  $z = 0$ , or both. As some sort of interpretation, it is to be remembered that  $t = 0$  signifies that the occurrence of any particle in the volume is highly improbable, i.e. there is an infinite rarefaction of matter in the volume, and so the probability of occurrence of non-zero value of  $M$  is very small, i.e. zero. Similarly  $z = 0$  corresponds to infinite rarefaction of energy, and so  $P(t, z)$  for finite non-zero value of  $E$  is obviously zero. Again  $t = 1$  and  $z = 1$  can be similarly interpreted as the case of infinite accumulation of matter and energy respectively in the volume, so  $P(t, z) = 0$ , when  $t = 1$ , or  $z = 1$ , or both, for finite values of  $E$  and  $M$ , as this is incompatible with the idea of infinite accumulation. Contrary to the cases  $z = 0$  or  $t = 0$ , for  $z = 1$  or  $t = 1$ , the form (1) does not give  $P(t, z) = 0$ . This has been introduced here as a sort of characteristic of the nature of the function  $P(t, z)$  to fulfil the physical requirements.

Moreover, as defined, the continuous and differentiable function  $P(t, z)$  is positive for all values of  $t, z$ , so  $P(t, z)$  must have at least one maximum within the domains of  $t$  and  $z$ .

V. SPECIFICATION OF VALUES OF  $t, z$  CORRESPONDING TO THE OBSERVED STATE.

Now, the probability of occurrence of  $E$  and  $M$  in any state, as given by (1), is

$$P(t, z) = \frac{W(E, M) \cdot t^M \cdot z^E}{f(t, z)}.$$

Then, the probability of occurrence of an observed state with the observed value of  $E_0$  and  $M_0$  is

$$P(t_0, z_0) = \frac{W(E_0, M_0) \cdot t_0^{M_0} \cdot z_0^{E_0}}{f(t_0, z_0)},$$

where  $t_0, z_0$  are such that for these values of  $t, z$ ,  $P(t, z)$  has a maximum with observed values of  $M$  and  $E$ . Then,  $t_0$  and  $z_0$  are given by the equations,

$$M_0 = t_0 \cdot \frac{\partial}{\partial t_0} \{ \log f(t_0, z_0) \} \quad \dots \quad \dots \quad \dots \quad (19)$$

and 
$$E_0 = z_0 \cdot \frac{\partial}{\partial z_0} \{ \log f(t_0, z_0) \}. \quad \dots \quad \dots \quad \dots \quad (20)$$

It is important to note the relation between  $M$  and  $E$  as specified in (19) and (20) with average values  $\bar{M}$  and  $\bar{E}$  obtained when  $t = t_0$  and  $z = z_0$ . One thus obtains,

$$\bar{M} = \frac{\sum \sum M \cdot W(E, M) \cdot t_0^M \cdot z_0^E}{\sum \sum W(E, M) \cdot t_0^M \cdot z_0^E} = t_0 \cdot \frac{\partial}{\partial t_0} \{ \log f(t_0, z_0) \},$$

and

$$\bar{E} = \frac{\sum \sum E \cdot W(E, M) \cdot t_0^M \cdot z_0^E}{\sum \sum W(E, M) \cdot t_0^M \cdot z_0^E} = z_0 \cdot \frac{\partial}{\partial z_0} \{ \log f(t_0, z_0) \}.$$

So average values  $\bar{M}$  and  $\bar{E}$  are identical with those  $M_0, E_0$  defined by (19) and (20) and so hereafter  $M, E$  will be replaced by  $M_0, E_0$  freely.

### VI. UNIQUENESS OF $t_0$ AND $z_0$ .

Now, to justify the correlation of  $t_0, z_0$  with physical properties of the system under consideration, it will be necessary to show that  $(t_0, z_0)$ , as defined by (19) and (20), is unique. For this,  $P(t, z)$  will be shown to have a unique maximum, which will be done by showing that every stationary value of  $P(t, z)$ , in the range of  $t, z$  mentioned above, must be a maximum of  $P(t, z)$ , and so  $P(t, z)$  being a single-valued function with continuous derivatives of first two orders cannot have more than one maximum of  $P(t, z)$ . To decide the nature of stationary values of  $P(t, z)$ , the function

$$\Phi(t, z) = \log P(t, z) \quad \dots \quad (21)$$

will be considered.

On expanding the function  $\Phi(t, z)$  about the values  $t_0, z_0$  by Taylor's theorem of two variables, one can write,

$$\begin{aligned} \Phi(t, z) = & \Phi(t_0, z_0) + \{ \Phi_{t_0 t_0} (t-t_0)^2 + 2 \cdot \Phi_{t_0 z_0} (t-t_0)(z-z_0) + \Phi_{z_0 z_0} (z-z_0)^2 \} \\ & + \{ \Phi_{t_0 t_0 t_0} (t-t_0)^3 + 3 \cdot \Phi_{t_0 t_0 z_0} (t-t_0)^2 (z-z_0) + 3 \cdot \Phi_{t_0 z_0 z_0} (t-t_0)(z-z_0)^2 \\ & + \Phi_{z_0 z_0 z_0} (z-z_0)^3 \} + \dots \dots \dots \quad (22) \end{aligned}$$

where  $t_0, z_0$  are defined by (19).

Now, by straightforward calculations it can be shown that

$$\begin{aligned} [\Phi_{tt}]_{t_0, z_0} = & -\frac{1}{t_0^2} \cdot \frac{1}{\{ f(t_0, z_0) \}^2} \\ & \times \left[ \sum \sum \sum \sum (M-M')^2 \cdot W(E, M) \cdot W(E', M') \cdot t_0^{M+M'} \cdot z_0^{E+E'} \right] < 0, \\ [\Phi_{zz}]_{t_0, z_0} = & -\frac{1}{z_0^2} \cdot \frac{1}{\{ f(t_0, z_0) \}^2} \\ & \times \left[ \sum \sum \sum \sum (E-E')^2 \cdot W(E, M) \cdot W(E', M') \cdot t_0^{M+M'} \cdot z_0^{E+E'} \right] < 0, \end{aligned}$$



and

$$\begin{aligned} \left| \frac{\Phi_{t_0 t_0} \Phi_{z_0 z_0}}{\Phi_{t_0 z_0} \Phi_{z_0 t_0}} \right| &= \frac{1}{t_0 \cdot z_0} \cdot \frac{1}{\{f(t_0, z_0)\}^2} \cdot \sum \sum \sum \sum \left| \frac{M-M'}{E-E'} \quad \frac{M''-M'''}{E''-E'''} \right|^2 \\ &\times W(E, M) \cdot W(E', M') \cdot W(E'', M'') \cdot W(E''', M''') \\ &\times t_0^{M+M'+M''+M'''} \\ &\times z_0^{E+E'+E''+E'''} \\ &> 0. \end{aligned}$$

So the expression within the bracket in the second term in (22) is negative definite. So  $\Phi(t, z)$  has maximum at  $(t_0, z_0)$  if  $(t_0, z_0)$  corresponds to a stationary value of the function. Thus,  $\Phi(t, z)$  and so  $P(t, z)$  have only one maximum. Thus  $(t_0, z_0)$  is the unique set.

VII. INFLUENCE OF VARIATIONS IN THE ENVIRONMENT.

The behaviour of the system in a definite environment has been investigated above. The statement that the system is in a definite environment implies the existence of some external parameters—other than the quantities already introduced—which are kept constant and so are not explicitly mentioned in previous discussions. It is easy to see that the volume of the system is one of the parameters; and the others may be the area of the boundary-walls when surface tension is significant, the intensity of current when the system is a portion of conducting medium, some parameters involved in the definition of the external field of forces if any, etc. These parameters will be denoted by  $x_i$ 's. Properties of the system in different virtual states, and the average properties will evidently depend on the values of these  $x_i$ 's. The effect of the variations in  $x_i$ 's on the average properties will be considered now. This consideration will be necessary to make the theory complete from the point of view of applications, as the influence of variations in environments on the behaviour of the system is of great importance for application to physics and other sciences.

With this object in view, we shall first consider such infinitesimal variation in the parameters  $x_i$ 's that due to this variation there is no change in  $M$ , the quantity of matter contained in the system. For actual physical system, the process of variations of the above type can be visualised if it is imagined that during the process of such variations the envelope of the system is replaced by a conducting one, which is introduced just before commencement of the process and is removed just after the process.<sup>1</sup> Then, if  $(M, E)$  be the mass and the energy in the virtual state of the system at commencement of the variation, then the equation of continuity for energy can be written as

$$dE = \sum \frac{\partial E}{\partial x_i} \cdot dx_i + d'q, \dots \dots \dots (23)$$

where  $\frac{\partial E}{\partial x_i}$ 's are values in the virtual state of the system <sup>2</sup> and  $d'q$  is the increase of the energy in the system which is not accounted for by the first term, viz. the increase due to flow of energy from outside in the system and other similar processes.

<sup>1</sup> Here, as in classical phenomenological thermodynamics, it is assumed that the system is not materially affected by introduction or removal of the walls.

<sup>2</sup> Here, it is implicitly assumed that there is a value of  $\partial E / \partial x_i$  for every virtual state specified by  $E, M$ . This will be more plausible if each virtual state of the system is looked upon as state of virtual system (replica).

Now, as which virtual state is the initial virtual state of the system cannot be determined, and as only average properties (which are here the same as those corresponding to the real state) of system are of real physical significance, so the equation (when there is no generation or annihilation of energy) should be written as

$$d\bar{E} = \sum_i \frac{\partial \bar{E}}{\partial x_i} \cdot dx_i + d'Q, \quad \dots \quad \dots \quad \dots \quad (24)$$

where  $d'Q$  is the *average* value of all  $d'q$ 's. This equation of continuity may be looked upon as a form of the first law of thermodynamics. Now

$$d'Q = d\bar{E} - \sum \frac{\partial \bar{E}}{\partial x_i} \cdot dx_i, \quad \dots \quad \dots \quad \dots \quad (25)$$

where

$$\begin{aligned} \left( - \frac{\partial \bar{E}}{\partial x_i} \right) &= \frac{\sum_{E=0}^{\infty} \sum_{M=0}^{\infty} \left( - \frac{\partial E}{\partial x_i} \right) \cdot W(E, M) \cdot t_0^M \cdot z_0^E}{\sum_{E=0}^{\infty} \sum_{M=0}^{\infty} W(E, M) \cdot t_0^M \cdot z_0^E} \\ &= \frac{1}{\log \frac{1}{z_0}} \cdot \frac{\partial}{\partial x_i} \{ \log \cdot f(t_0, z_0) \} \quad \dots \quad \dots \quad \dots \quad (26) \end{aligned}$$

as  $W(E, M)$  is independent of the external parameter.

Now, if the system after variation of environment be again allowed to the new state for sufficiently long time for establishment of the statistical equilibrium, then the 'real' state of the system in the definite environment (the altered environment) will be specified by two distribution-parameters, in general, different from  $t_0$  and  $z_0$ ; let them be  $t_0 + dt_0$  and  $z_0 + dz_0$ . Thus, the variation, considered above, is a very slow process from one equilibrium state to another and can easily be recognised as the usual reversible variations of thermodynamics. For this variation, when both sides of the equation (24) are multiplied by  $\left( \log \frac{1}{z_0} \right)$ , the relation becomes

$$\begin{aligned} \left( \log \frac{1}{z_0} \right) \cdot d'Q &= \left( \log \frac{1}{z_0} \right) \cdot \left\{ d\bar{E} - \sum \frac{\partial \bar{E}}{\partial x_i} \cdot dx_i \right\} \\ &= \left( \log \frac{1}{z_0} \right) \cdot d\bar{E} + \sum_i \frac{\partial}{\partial x_i} \{ \log f(t_0, z_0) \} \cdot dx_i \\ &= d \left\{ \left( \log \frac{1}{z_0} \right) \cdot \bar{E} \right\} + \sum_i \frac{\partial}{\partial x_i} \cdot \{ \log f(t_0, z_0) \} dx_i \\ &\quad + \frac{\partial}{\partial z_0} \{ \log f(t_0, z_0) \} dz_0 \\ &= d \left\{ \left( \log \frac{1}{z_0} \right) \cdot \bar{E} + \log f(t_0, z_0) \right\} - \frac{\partial}{\partial t_0} \{ \log f(t_0, z_0) \} \cdot dt_0 \\ &= d \left\{ \left( \log \frac{1}{z_0} \right) \cdot E + \log f(t_0, z_0) - N \cdot \log t_0 \right\} \quad \dots \quad \dots \quad (27) \end{aligned}$$

This shows that  $\left(\log \frac{1}{z_0}\right)$  is the integrating factor of  $d'Q$ , and the integral can only be determined for finite reversible variations composed of infinitesimal variations.

The integrating factor  $\left(\log \frac{1}{z_0}\right)$  of the equation is to be taken to be proportional to  $\frac{1}{kT}$  and, after choice of scale, one can write,

$$z_0 = e^{-\frac{1}{kT}}, \quad \dots \dots \dots (28)$$

and  $S$ , the corresponding integral, is, as usual, to be interpreted as the entropy of the system and is given by

$$\frac{dS}{k} = \frac{d'Q}{kT} = d \left[ \frac{E}{kT} + \log F(t_0, T) - N \cdot \log t_0 \right], \quad \dots \dots (29)$$

where

$$F(t_0, T) = f(t_0, z_0). \quad \dots \dots \dots (30)$$

Then,

$$S = \frac{E}{T} + k \cdot \log F(t_0, T) - N \cdot k \cdot \log t_0 + S_0. \quad \dots \dots (31)$$

If the concept of absolute entropy is introduced after Planck, then,

$$S_0 = 0, \quad \dots \dots \dots (32)$$

and

$$S = \frac{E}{T} + k \cdot \log F(t_0, T) - Nk \cdot \log t_0 \quad \dots \dots \dots (33)$$

Then,

$$\Psi = k \cdot \log F(t_0, T) - Nk \cdot \log t_0. \quad \dots \dots \dots (34)$$

$d'Q = T \cdot dS$  can now be easily interpreted as heat supplied to the system.

$d\bar{E}$  is the change of total energy. Then,  $-\sum \frac{\partial \bar{E}}{\partial x_i} \cdot dx_i$  can be interpreted as the external work done by the system. Thus, if the generalised forces on the system be taken as  $X_i$ , then one obtains

$$X_i = \frac{\partial \bar{E}}{\partial x_i} \cdot \dots \dots \dots (35)$$

Thus, if the system under consideration be taken as of the mechanical (classical or quantum) nature, then the equation can be recognised as the usual equation of the principle of adiabatic invariance, which principle has been discussed for systems of classical and quantum mechanics by Boltzmann (1866), Clausius (Routh, 1905), Einstein (Sommerfeld, 1923), Born (1927) and others from completely different considerations.

VIII. INTRODUCTION OF CONCEPT OF CHEMICAL POTENTIAL.

Now, as in the above section, the equation of continuity of matter (after proper averaging) can be written as

$$d\bar{M} = \sum \frac{\partial \bar{M}}{\partial x_i} \cdot dx_i + d'm, \quad \dots \dots \dots (36)$$

where  $d'm$  is the quantity of matter flowing into the volume. ( $E$  is kept constant in variation, as some variables are to be kept constant such that this can be recognised as the previous system.)

Now, as before, one obtains

$$\begin{aligned}
 -\frac{\partial \bar{M}}{\partial x_i} &= \frac{\sum_{E=0}^{\infty} \sum_{M=0}^{\infty} \left(-\frac{\partial M}{\partial x_i}\right) \cdot W(E, M) \cdot t_0^M \cdot z_0^E}{\sum_{E=0}^{\infty} \sum_{M=0}^{\infty} W(E, M) \cdot t_0^M \cdot z_0^E} \\
 &= \frac{1}{\log \frac{1}{t_0}} \cdot \frac{\partial}{\partial x_i} \{ \log \cdot f(t_0, z_0) \} \dots \dots \dots (36A)
 \end{aligned}$$

Then,

$$\begin{aligned}
 \left(\log \frac{1}{t_0}\right) \cdot d'm &= \left(\log \frac{1}{t_0}\right) \cdot \left[ d\bar{M} - \sum \frac{\partial \bar{M}}{\partial x_i} \cdot dx_i \right] \\
 &= d \left\{ \left(\log \frac{1}{t_0}\right) \cdot \bar{M} \right\} + \sum \frac{\partial}{\partial x_i} \left\{ \log \cdot f(t_0, z_0) \right\} dx_i + \frac{\partial}{\partial t_0} \left\{ \log f(t_0, z_0) \right\} dz_0 \\
 &= d \left\{ \left(\log \frac{1}{t_0}\right) \cdot \bar{M} + \log f(t_0, z_0) \right\} - \frac{\partial}{\partial z_0} \left\{ \log f(t_0, z_0) \right\} dz_0 \\
 &= d \left\{ \left(\log \frac{1}{t_0}\right) \cdot \bar{M} + \log f(t_0, z_0) - E \cdot \log z_0 \right\} \\
 &= \frac{1}{k} \cdot dS \dots \dots \dots (37)
 \end{aligned}$$

Now,  $d'm$  is the increase of  $M$  not due to any change of parameter and so due to flow, then,

$$\log t_0 = -\frac{1}{k} \left( \frac{\partial S}{\partial \bar{M}} \right)_{E, x_i} = -\frac{1}{k} \left( \frac{\partial S}{\partial \bar{M}} \right)_{E, x_i} \dots \dots (38)$$

$$= \frac{\mu'}{mkT} = \frac{\mu}{kT}, \dots \dots \dots (39)$$

where  $\mu$  is usual chemical potential,  $m$  being mass of the constituent particle. From the above discussions, it follows that the equations of continuity of energy and matter lead to the same integral, i.e., the entropy. Thus, so far as definition of entropy is concerned, the energy and the matter have the same rôle. From the present general discussion of the thermodynamic problem it is clear that the special stress on the significance of energy in usual discussions of thermodynamics is not necessary in mathematical developments. Also, it is to be noted that in the present discussion no specific assumption about the properties of energy and matter, other than the laws of conservations and the possibility of variation with external parameters, has been used. Now, in the present discussion,  $t_0$  and  $z_0$  have been introduced as *a priori* probabilities that unit quantities of mass and energy occur in the specified volume. From the macroscopic point of view, it is known that the flow of energy is controlled by temperature, and the transfer of mass by chemical potential, so relations between  $t_0$  and  $\mu$ ,  $z_0$  and  $T$ , as obtained here, are quite satisfactory.

IX. INCREASING PROPERTY OF ENTROPY.

From section VII we have,

$$S = -\log \cdot \frac{t_0^M \cdot z_0^E}{f(t_0, z_0)} \dots \dots \dots (40)$$

It has been proved in sections V and VI that the argument of the logarithm in the equation (40) has one unique maximum for values  $t_0$  and  $z_0$  of  $t$  and  $z$ . So the function  $S(t, z)$  has a unique minimum for values of  $t_0$  and  $z_0$ .

Let us consider two isolated systems of some constituent parts, and let  $(t'_0, z'_0)$  and  $(t''_0, z''_0)$  determine their states respectively. Let  $E'$  and  $E''$  be their total energies, and  $M'$ ,  $M''$  be number of constituent parts respectively. Then their entropies,  $S'(t'_0, z'_0)$  and  $S''(t''_0, z''_0)$ , are given by

$$S'(t'_0, z'_0) = -\log \frac{t_0^{M'} \cdot z_0^{E'}}{f'(t'_0, z'_0)}, \dots \dots \dots (41)$$

$$S''(t''_0, z''_0) = -\log \frac{t_0^{M''} \cdot z_0^{E''}}{f''(t''_0, z''_0)}, \dots \dots \dots (42)$$

where the functions  $S'$ ,  $S''$  have unique minimum, i.e., for  $(t'_0, z'_0)$  and  $(t''_0, z''_0)$  respectively, i.e.,

$$S'(t, z) \geq S'(t'_0, z'_0), \dots \dots \dots (43)$$

and

$$S''(t, z) \geq S''(t''_0, z''_0), \dots \dots \dots (44)$$

where  $(t, z)$  be any other set of values.

If the systems be coupled in any manner provided that both the systems, taken together, remain isolated, i.e. there is no loss of energy and matter in the total system, then,

$$E = E' + E'', \dots \dots \dots (45)$$

$$M = M' + M'', \dots \dots \dots (46)$$

where  $E$ ,  $M$  are energy and mass of the total system.

Let  $(t_0, z_0)$  define the state of the compound system after the statistical equilibrium has been set in. Then the entropy is given by

$$\begin{aligned} S(t_0, z_0) &= -\log \frac{t_0^M \cdot z_0^E}{f(t_0, z_0)} = -\log \left[ \frac{t_0^{M'} \cdot z_0^{E'}}{f'(t_0, z_0)} \cdot \frac{t_0^{M''} \cdot z_0^{E''}}{f''(t_0, z_0)} \right] \\ &= -\log \frac{t_0^{M'} \cdot z_0^{E'}}{f'(t_0, z_0)} - \log \frac{t_0^{M''} \cdot z_0^{E''}}{f''(t_0, z_0)} \\ &= S'(t_0, z_0) + S''(t_0, z_0) \\ &\geq S'(t'_0, z'_0) + S''(t''_0, z''_0) \dots \dots \dots (47) \end{aligned}$$

[by (44) and (18)].

Thus the entropy of a closed system cannot decrease.

X. LAWS OF MICROSCOPIC DISTRIBUTIONS.

The previous discussions are mainly of microscopic nature and no assumption has been made about the nature of the constituent parts of the system. It will be now shown the usual laws for microscopic distributions can also be simply deduced in the present discussions, if the usual hypothesis about the microscopic nature of the system be made. So the system under consideration will be assumed to be composed of a large number of small constituent parts, viz. molecules, atoms, ions, etc. Let us write

$$w(E, N) = W(E, M). \quad \dots \quad \dots \quad \dots \quad (48)$$

Let the energy of one of the microscopic state of constituent parts be denoted by  $\epsilon_r$ , and let  $n_r$  be the number of constituent particles in the state at any instant. In statistical considerations, the expected value  $\bar{n}_r$  of  $n_r$  is of real interest and is to be calculated. Now, the number of ways in which a particular value  $n_r$  with energy  $\epsilon_r$  is realised when the total energy of the system is  $E$  and the total number of constituent parts is  $N$ , is denoted by  $w'(E - n_r \epsilon_r, N - n_r)$ , then  $w'(E - n_r \epsilon_r, N - n_r)$  denotes the number of ways in which  $E - n_r \epsilon_r$  can be partitioned in  $N - n_r$  parts, such that no one of the parts is equal to  $\epsilon_r$ . Then, on writing  $t_1 = t_0^m$ , the expected value  $\bar{n}_r$  is given by

$$\begin{aligned} \bar{n}_r &= \frac{\sum_{E=0}^{\infty} \sum_{M=0}^{\infty} \sum_{n_r=0}^N n_r \cdot w'(E - n_r \epsilon_r, N - n_r) \cdot t_1^N \cdot z_0^E}{\sum_{E=0}^{\infty} \sum_{N=0}^{\infty} w(E, N) \cdot t_1^N \cdot z_0^E} \\ &= \frac{\left( \sum_{n_r=0}^{\infty} n_r \cdot t_1 \cdot z_0^{n_r \epsilon_r} \right) \left[ 1 + \sum_{N=0}^{\infty} \sum_{E=0}^{\infty} w'(E - n_r \epsilon_r, N - n_r) \cdot t_1^N \cdot z_0^E \right]}{\left( 1 + \sum_{n_r=0}^{\infty} t_1^{n_r} \cdot z_0^{n_r \epsilon_r} \right) \left[ 1 + \sum_{N=0}^{\infty} \sum_{E=0}^{\infty} w'(E - n_r \epsilon_r, N - n_r) \cdot t_1^N \cdot z_0^E \right]} \\ &= \frac{t_1 \cdot \frac{\partial}{\partial t_1} \left( 1 + \sum_{n_r=0}^{\infty} t_1^{n_r} \cdot z_0^{n_r \epsilon_r} \right)}{\left( 1 + \sum_{n_r=0}^{\infty} t_1^{n_r} \cdot z_0^{n_r \epsilon_r} \right)} = t_1 \cdot \frac{\partial}{\partial t_1} \left\{ \log g_r(t_0, z_0) \right\}. \quad \dots \quad \dots \quad (49) \end{aligned}$$

Now,

$$1 + \sum_{n_r=0}^{\infty} t_0^{n_r} \cdot z_0^{n_r \epsilon_r}$$

is one of the generating functions as discussed in Section IV, and is denoted by  $g_r(t_0, z_0)$ .

$$\therefore \bar{n}_r = t_1 \cdot \frac{\partial}{\partial t_1} \left\{ \log g_r(t_0, z_0) \right\}. \quad \dots \quad \dots \quad \dots \quad (50)$$

Then, in the case of the system composed of Bose particles :

$$g_r(t_0, z_0) = \left\{ 1 + \sum_{n_r=1}^{\infty} t_0^m \cdot z_0^{n_r \epsilon_r} \right\} = \left\{ \frac{1}{1 - t_0^m z_0^{\epsilon_r}} \right\}^{A_r}$$

$$\therefore \bar{n}_r = \frac{A_r}{t_0^{-m} \cdot z_0^{-\epsilon_r} - 1} = \frac{A_r}{e^{\frac{m\mu + \epsilon_r}{kT}} - 1} \dots \dots \dots (51)$$

In the case of the system composed of Fermi-Dirac particles:

$$g_r = \left( 1 + t_0^m z_0^{\epsilon_r} \right)^{A_r}$$

$$\therefore \bar{n}_r = \frac{A_r}{t_0^{-m} \cdot z_0^{-\epsilon_r} + 1} = \frac{A_r}{e^{\frac{m\mu + \epsilon_r}{kT}} + 1} \dots \dots (52)$$

In the case of the system composed of Gentile's particles:

$$g_r = \left\{ \frac{1 - t_0^{m(d+1)} \cdot z_0^{\epsilon_r(d+1)}}{1 - t_0^m z_0^{\epsilon_r}} \right\}^{A_r}$$

$$\therefore \bar{n}_r = A_r \left\{ \frac{1}{t_0^{-m} \cdot z_0^{-\epsilon_r} - 1} - \frac{(d+1)}{t_0^{-m(d+1)} \cdot z_0^{-(d+1)\epsilon_r} - 1} \right\}$$

$$= A_r \left\{ \frac{1}{e^{\frac{m\mu + \epsilon_r}{kT}} - 1} - \frac{(d+1)}{e^{\frac{(d+1)(m\mu + \epsilon_r)}{kT}} - 1} \right\} \dots \dots (53)$$

In the case of the classical system:

$$g_r = e^{A_r \cdot t_0^m \cdot z_0^{\epsilon_r}}$$

$$\therefore \bar{n}_r = A_r \cdot t_0^m \cdot z_0^{\epsilon_r} = A_r \cdot e^{\frac{m\mu + \epsilon_r}{kT}} \dots \dots \dots (54)$$

XI. FLUCTUATIONS.

As fluctuation of average properties is a most important concept of statistical thermodynamics, the usual results will be deduced here before concluding the discussion. Now,

$$\bar{E}^2 = \frac{\sum_{E=0}^{\infty} \sum_{M=0}^{\infty} E^2 \cdot W(E, M) \cdot t_0^M \cdot z_0^E}{\sum_{E=0}^{\infty} \sum_{M=0}^{\infty} W(E, M) \cdot t_0^M \cdot z_0^E} = \frac{1}{\{f(t_0, z_0)\}} \cdot \left\{ z_0 \frac{\partial}{\partial z_0} \right\}^2 \cdot \{f(t_0, z_0)\}$$

$$\bar{E}^2 = \frac{1}{f(t_0, z_0)} \cdot \left\{ z_0 \frac{\partial}{\partial z_0} \right\} \cdot \left\{ \bar{E} \cdot f(t_0, z_0) \right\} = \bar{E}^2 + z_0 \cdot \frac{\partial \bar{E}}{\partial z_0}$$

$$\therefore (\overline{E - \bar{E}})^2 = \bar{E}^2 - \bar{E}^2 = \frac{\partial \bar{E}}{\partial (\log z_0)} = k \cdot T^2 \cdot c_v$$

$$\therefore \frac{(\overline{E - \bar{E}})^2}{\bar{E}^2} = \frac{kT^2 \cdot c_v}{\bar{E}^2} = \frac{kT^2 c_v}{E^2} \dots \dots \dots (55)$$

Similarly,

$$\begin{aligned} \overline{M^2} &= \frac{\sum_{E=0}^{\infty} \sum_{M=0}^{\infty} M^2 \cdot W(E, M) \cdot t_0^M \cdot z_0^E}{\sum_{E=0}^{\infty} \sum_{M=0}^{\infty} W(E, M) \cdot t_0^M \cdot z_0^E} \\ &= \frac{1}{f(t_0, z_0)} \cdot \left\{ t_0 \cdot \frac{\partial}{\partial t_0} \right\}^2 \cdot \left\{ f(t_0, z_0) \right\} = \frac{1}{f(t_0, z_0)} \cdot \left\{ t_0 \cdot \frac{\partial}{\partial t_0} \right\} \cdot \left\{ \overline{M} \cdot f(t_0, z_0) \right\} \\ &= \overline{M^2} + t_0 \cdot \frac{\partial \overline{M}}{\partial t_0} \\ \therefore \overline{(M - \overline{M})^2} &= \overline{M^2} - \overline{M}^2 = \frac{\partial \overline{M}}{\partial \left( \frac{\mu}{kT} \right)} = kT \cdot \frac{\partial \overline{M}}{\partial \mu} \\ \therefore \frac{\overline{(M - \overline{M})^2}}{\overline{M^2}} &= \frac{\overline{M^2} - \overline{M}^2}{\overline{M^2}} = \frac{kT}{\overline{M^2}} \cdot \frac{\partial \overline{M}}{\partial \mu} \\ \therefore \frac{\overline{(N - \overline{N})^2}}{\overline{N^2}} &= \frac{kT}{\overline{N^2} \cdot m} \cdot \frac{\partial \overline{N}}{\partial \mu} \dots \dots \dots \dots \dots \dots \dots \dots \dots (56) \end{aligned}$$

Also one can obtain

$$\begin{aligned} \overline{n_r^2} &= \frac{\sum_{N=0}^{\infty} \sum_{E=0}^{\infty} \sum_{n_r=0}^N n_r^2 \cdot w'(E - n_r \epsilon_r, N_r - n_r) \cdot t_1^N \cdot z_0^E}{\sum_{N=0}^{\infty} \sum_{E=0}^{\infty} w(E, N) \cdot t_1^N \cdot z_0^E} \\ &= \frac{1}{g_r(t_0, z_0)} \cdot \left\{ t_1 \cdot \frac{\partial}{\partial t_1} \right\}^2 \cdot \left\{ g_r(t_0, z_0) \right\}, \\ \overline{n_r^2} &= \overline{n_r}^2 + t_1 \cdot \frac{\partial}{\partial t_1} \cdot (\overline{n_r}) \\ \therefore \overline{(n_r - \overline{n_r})^2} &= \overline{n_r^2} - \overline{n_r}^2 = t_1 \cdot \frac{\partial}{\partial t_1} (\overline{n_r}) = \frac{kT}{m} \cdot \frac{\partial \overline{n_r}}{\partial \mu} \\ \therefore \frac{\overline{(n_r - \overline{n_r})^2}}{\overline{n_r^2}} &= \frac{kT}{\overline{n_r^2} \cdot m} \cdot \frac{\partial \overline{n_r}}{\partial \mu} \dots \dots \dots \dots \dots \dots \dots \dots \dots (57) \end{aligned}$$

These are the usual formulae found in the treatises of Fowler (1936) and Tolman (1938).

XII. CONCLUSION.

In the above discussion, all usual results have been derived in the forms obtained by Fowler (1936). Also some subsidiary mathematical calculations are the same as those of Fowler. But the present method differs from that of Fowler



almost in all the essential points, of which the most important ones may be summarised in the following:

- (i) Here the entire discussion is based on a principle similar to the principle of maximum likelihood, whereas in Fowler's method the same is based on average properties.
- (ii) Here no approximation formula has been used, whereas in the latter, the approximation by the method of steepest descent is the kernel of the entire development.
- (iii) Here a parameter or a variable, which has no *ab initio* significance (physical or statistical), has never been introduced and so all quantities entering in the calculations are real; whereas, in the other, two parameters, which have been afterwards correlated to two important functions of thermodynamics, have been introduced as two complex quantities, helping the calculations of approximate values and so having no *ab initio* significance.

In the present investigation, the entire discussion of the behaviour of a thermodynamic system is made consistently with the general formalism of statistics. In this discussion, there is nothing which will restrict it to the thermodynamic systems only. So it is expected that the present method can be applied for discussions of essentially different types, viz. the problem of distributions of population and money in a country where  $M$  and  $E$  will represent the measure of the population and the money in the country.

Moreover it should be noted that the method, developed here, is essentially statistical and macroscopic, but can be applied to microscopic discussion with equal convenience and advantage.

#### ABSTRACT.

In this paper, an essentially statistical approach has been made to investigate the behaviour of a thermodynamic system. In the entire development, the problem has been discussed macroscopically as a statistical problem of general type. As in phenomenological thermodynamics, no assumption about the structure and the internal mechanism of the system has been introduced. For this, a probability of occurrence of the system, enclosed in a definite volume surrounded by a definite environment, in a state specified by definite values for quantities of matter and energy contained by it, is suitably defined and is taken to be the starting point of the present discussion. The analytical behaviour of the probability, considered as a function of two parameters—the characteristic parameters of distribution—has been investigated and it has been shown that this function has a unique maximum for a set of values of distribution-parameters controlling the energy-exchange and the matter-exchange with the environment. It has been assumed that the state, for which the probability of occurrence is a maximum, corresponds to the observed state, and the values of the distribution-parameters, corresponding to the maximum value of the probability, are taken to specify the state of the system in a definite environment. Thus, over and above, the unique set of values for quantities of matter and energy, a probability-distribution of matter and energy has been associated to every observed state of the system. After this, to consider the effect of variations in the environment of the system, the equation of continuity for energy and matter has been taken in suitable form. Some functions associated with the equation of continuity for energy (the first law of thermodynamics) and that of matter, have been identified as entropy, temperature, and the chemical potential of the system. In this connection, some discussions about reversible variations and about the principle of adiabatic invariance have been made. The non-decreasing properties of the entropy have been established. Usual formulae for fluctuations have been easily obtained. It has also been shown that the method is also suitable for obtaining the laws of microscopic distribution when usual assumptions about microscopic nature of the system are introduced.

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