AN ESSENTIALLY STATISTICAL APPROACH TO THERMODYNAMIC PROBLEM—II

by M. Dutta, *Research Fellow, N.I.S.I., Khaira Laboratory of Physics, College of Science and Technology, Calcutta*

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Introduction

In a recent paper * (1953) the author has stressed the necessity of an essentially statistical approach to the thermodynamic problems and has developed a general statistical method for investigating thermodynamic behaviour of a system. There, for simplicity, the system has been assumed to be composed of matter of (chemically) single type, and the contribution of radiation energy, if any, in the behaviour of the system has been taken to be negligibly insignificant. In the present paper, the proposed statistical method will be shown to be equally suitable for investigations of thermodynamic behaviour of system of different types, viz. those of black-body radiations, those of free radiation and matter of single chemical types, and those of matter of chemically different types. In agreement with other usual theories and with the assumptions of the paper I, it is assumed that the amount of energy and matter can only be discrete. In every case, the usual formulae, as given by Fowler (1936), Tolman (1946) and others, have been obtained.

Part I. An Assembly of Free Radiation

1. *Formulation of Problem: The Law of Probability-distribution*

Here, the system means a definite amount of energy E, in the form of free radiation in a definite volume in a definite environment. As in the paper I, the system is to be taken as open, i.e. there is no hindrance of energy-exchange between the system and the environment. Now, since there is no question of matter-exchange in this case with the environment, so in consistency with the trend of discussions made in the paper I, only one a priori probability z for each unit of energy to be in the volume under consideration will be introduced. Then, the probability of occurrences of a system in a state specified by E is given by

$$P(z, E) = \frac{W(E)z^E}{\sum\limits_{E=0}^{\infty} W(E)z^E} = \frac{W(E)z^E}{f(z)}, \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where

$$f(z) = \sum_{E=0}^{\infty} W(E)z^E \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

The above may be looked upon as a form of Baye's theorem. As before, for determining z in agreement with the usual ideas of statistical equilibrium, the 'real' value E_0 (taken to be known in the sense of classical thermodynamics) corresponds

* This paper will be referred to as the paper I in the present discussion.

to the maximum value of the probability of occurrence $P(z, E)$, considered as a function of z. Thus, here as mentioned in the paper I, the estimation of parameter is similar to that principle of maximum likelihood.

2. *Behaviour of the Function $W(E), f(z), P(z, E)$*

If, as usual, it assumed that the assembly is composed of photons and that any number of photons can have same energy, then evidently $W(E)$ is partitions of E into any number of parts having values in the set, $\epsilon_0, \epsilon_1, \ldots \epsilon_n, \ldots$ Then, the generating function is given by

$$f(z) = \prod_n \left(1-z^{\epsilon_n}\right)^{A_n}, \qquad \ldots \qquad (3)$$

where A_n is degeneracy of ϵ_n-energy state. Thus, $f(z)$ is expressible in form of infinite products and z lies between 0 and 1, so, continuity, differentiability, etc. follow simply from the well-known properties of infinite products.

Now, again, for $z = 0$, i.e. the case of infinite dilution or the case where the condition of environment is such that the occurrence of free radiation-energy is highly improbable in the volume, the probability of occurrence of amount of energy $P(z, E) = 0$; and for $z = 1$, i.e. the case of infinite condensation or the case where the condition of environment is such that the occurrence of every amount of free radiation-energy in the volume is almost certain, then the probability of occurrence of only a finite amount of energy in the volume $P(z, E) = 0$. Therefore $P(z, E)$ must have at least one maximum, since $P(z, E) \geqslant 0$ always.

3. *Specification of z_0 and its Uniqueness*

Now, as in the paper I, z_0 corresponding to the stationary value is given by

$$E_0 = z_0 \frac{\partial}{\partial z_0} \{\log f(z_0)\}. \qquad \ldots \qquad (4)$$

Again, if one calculates $\bar{E}$ as

$$\bar{E} = \frac{\sum_E W(E) E z_0^E}{\sum_E W(E) z_0^E} = z_0 \frac{\partial}{\partial z_0} \{\log f(z_0)\} = E_0, \qquad \ldots \qquad (5)$$

so as in the paper I, the mean and the most probable values become equal for the present probability-distribution.

Now,

$$\begin{aligned} \Phi(z) &= \log P(z) \\ &= \Phi(z_0) + \frac{1}{2!}\Phi_{z_0z_0}(z-z_0)^2 + \frac{1}{3!}\Phi_{z_0z_0z_0}(z-z_0)^3 + \ldots, \qquad \ldots \qquad (6) \end{aligned}$$

where

$$\begin{aligned} \Phi_{z_0z_0} &= \frac{E}{z_0^2} - \frac{f_{z_0z_0}f - f_{z_0}^2}{f^2} \\ &= -\frac{1}{z_0} \frac{\left\{\Sigma E^2 W(E) z_0^E\right\}\left\{\Sigma W(E') z_0^{E'}\right\} - \left\{\Sigma E W(E) z_0^E\right\}\left\{\Sigma E' W(E') z_0^{E'}\right\}}{f^2} \\ &= -\frac{1}{z_0} \frac{\Sigma\Sigma (E-E')^2 W(E) W(E') z^{E+E'}}{f^2} \\ &\ngtr 0, \qquad \ldots \qquad (7) \end{aligned}$$

Thus, $\Phi(z)$, i.e. $P(z, E)$, has only one maximum. Therefore z_0 is the unique value of z corresponding to the stationary state.

4. *Influence of Variations of Environments*

Now as in the paper I, if the variations of parameters, involved in the definitions of the environments, be taken into account, then the equation of continuity of energy after usual averaging can be written as

$$\overline{dE} = \sum_i \frac{\overline{\partial E}}{\partial x_i} dx_i + d'Q, \quad \ldots \quad (8)$$

where

$$\left(-\frac{\overline{\partial E}}{\partial x_i}\right) = \frac{\sum\limits_{E=0}^{\infty} \left(-\frac{\partial E}{\partial x_i}\right) W(E) z_0^E}{\sum\limits_{E=0}^{\infty} W(E) z_0^E} = -\frac{1}{\left(\log \frac{1}{z_0}\right)} \cdot \frac{\partial}{\partial x_i} \{\log f(z_0)\} \quad \ldots \quad (9)$$

Now

$$\left(\log \frac{1}{z_0}\right) d'Q = \left(\log \frac{1}{z_0}\right) \left\{ \overline{dE} - \sum_i \frac{\overline{\partial E}}{\partial x_i} dx_i \right\}$$

$$= d\left\{\left(\log \frac{1}{z_0}\right) \bar{E}\right\} + \sum_i \frac{\partial}{\partial x_i} \{\log f(z_0)\} \, dx_i + \frac{\partial}{\partial z_0} \{\log f(z_0)\}$$

$$= d\left\{\left(\log \frac{1}{z_0}\right) \bar{E} + \log f(z_0)\right\} \quad \ldots \quad (10)$$

Then, on putting

$$z_0 = e^{-\frac{1}{kT}}, \quad \ldots \quad (11)$$

after choosing the scale properly as in the paper I, one has

$$dS = d\left\{\frac{E}{T} + k \log F(T)\right\}. \quad \ldots \quad (12)$$

5. *Laws of Microscopic Distributions*

Now, here if the radiation be assumed to be composed of the photon and if number of ways in which a particular n_ν (number of photons) with energy ϵ_ν be realised when the total energy of the system E is denoted by $w'(E - n_\nu \epsilon_\nu)$, then the expected value of $\bar{n}_\nu$ is given by

$$\bar{n}_\nu = \frac{\sum\limits_{E=0}^{\infty} \sum\limits_{n_\nu=0} n_\nu w'(E - n_\nu \epsilon_\nu) z_0^E}{\sum\limits_{E=0}^{\infty} W(E) z_0^E}$$

$$= \frac{\left(\sum\limits_{n_\nu=0}^{\infty} n_\nu z_0^{n_\nu \epsilon_\nu}\right)\left[1 + \sum\limits_{E}^{\infty} w'(E) z_0^E\right]}{\left(\sum\limits_{n_\nu=0}^{\infty} z_0^{n_\nu \epsilon_\nu}\right)\left[1 + \sum\limits_{E}^{\infty} w'(E) z_0^E\right]}$$

$$= z_0^{\epsilon_\nu} \frac{\partial}{\partial(z_0^{\epsilon_\nu})} \left\{ \log \left(1 + \sum_{n_\nu}^{\infty} z_0^{n_\nu \epsilon_\nu} \right) \right\} \quad .. \quad .. \quad .. \quad (13)$$

Then, the spectral-distribution of energy becomes

$$\bar{n}_\nu = \frac{A_\nu z_0^{\epsilon_\nu}}{1 - z_0^{\epsilon_\nu}} = \frac{A_\nu}{e^{\epsilon_\nu / kT}}. \quad .. \quad .. \quad .. \quad .. \quad (14)$$

This is the well-known Planck's law.

Remarks

Now, the assumption of existence of $W(E)$, the total number of realizations in which E can be realized in different ways in different frequencies, implies the exchange of energies amongst different frequencies, i.e. the existence of some matter in contact with the system consisting of radiation under consideration has been tacitly assumed. So, the present case is the case of black-body radiation.

Part II. An Assembly consisting of Radiation and Matter

1. *Description of Assembly*

Here, as in the paper I, a system in a definite thermodynamic state will mean a definite amount of energy and a definite amount of matter observed (in the sense of classical thermodynamics) in a definite volume in a definite environment. Here, as in the paper I, the system will be taken to be open with respect to energy and matter. Of course, for simplicity at present, the system will be assumed to be composed of (chemically) single type of material.

Now, as before, a constant a priori probability for a unit quantity of energy to exist in the volume and another constant a priori probability for a unit quantity of matter to exist in the volume will be introduced. Then, the probability of occurrence of the system in a state specified by E and M is given by

$$P(t, z, M, E) = \frac{W(E, M) t^M z^E}{\sum_E \sum_M W(E, M) t^M z^E} = \frac{W(E, M) t^M z^E}{f(t, z)}, \quad .. \quad .. \quad (15)$$

where

$$f(t, z) = \sum_E \sum_M W(E, M) t^M z^E. \quad .. \quad .. \quad .. \quad (16)$$

This expression is same as that in the previous paper (Dutta, 1953). The only difference is that here $W(E, M)$ can always be written as

$$\sum_{E_1 + E_2 = E} W_1(E_1) W_2(E_2, M) = W(E, M), \quad .. \quad .. \quad (17)$$

where E_1 is the amount of energy in the form of free radiation and E_2 that as the energy of matter. Obviously $W_1(E_1)$ is the function used in the part I of this paper and $W_2(E_2)$ is that used in the paper I. Then, from the theorem, stated and proved in the paper I, one gets

$$f(t, z) = f_1(z) f_2(t, z). \quad .. \quad .. \quad .. \quad .. \quad (18)$$

As before, the distribution-parameters t, z corresponding to the real values of E_0, M_0 (taken to be known from the observations in classical sense) are to be specified from the principle that the real values of E_0 and M_0 correspond to the maximum of the probability of occurrence considered as function of t and z.

Specification and Uniqueness of t_0 and z_0, etc.

In this case, equations specifying values of t_0 and z_0 and calculations showing the uniqueness of specified values and discussions of the effects of variations in the environments are same in the previous paper and so are not repeated here.

Laws of Microscopic Distributions

The previous discussions are mainly of microscopic nature and have been put forward without any specific assumptions about the microscopic nature of the system. Here, matter will be assumed to be composed of molecules and radiation of photons. As stated in the paper I, E_1 and E_2 are both to be taken as discrete. Let us write

$$w(E, N) = W(E, M) = w_1(E_1)\, w_2(E_2, N). \qquad \ldots \quad \ldots \quad (19)$$

Let ϵ_ν be the energy of one of the micro-energy state of photons and n_ν be the number of photons with energy ϵ_ν at any instant. Then, on writing

$$t_0' = t_0^m, \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (20)$$

one gets

$$\begin{aligned} n_\nu &= \frac{\sum_{E=0}^{\infty} \sum_{N=0}^{\infty} \sum_{n_\nu=0} n_\nu w_1'(E_1 - n_\nu \epsilon_\nu)\, w_2(E_2, N)\, t_0'^N z_0^E}{\sum_{\substack{E=0 \\ E_1+E_2=0}}^{\infty} \sum_{N=0}^{\infty} w_1'(E_1)\, w_2'(E_2, N)\, t_0'^N z_0^E} \\ &= \frac{\left(\sum_{n_\nu=0}^{\infty} n_\nu z_0^{n_\nu \epsilon_\nu}\right)\left[1 + \sum w_1'(E_1)\, w_2'(E_2, N)\, t_0'^N z_0^E\right]}{\left(1 + \sum_{n_\nu=1}^{\infty} z_0^{n_\nu \epsilon_\nu}\right)\left[1 + \sum\sum w_1'(E_1)\, w_2'(E_2, N)\, t_0'^N z_0^E\right]} \\ &= z_0^{\epsilon_\nu} \frac{\partial}{\partial z_0^{\epsilon_\nu}} \left\{\log\left(1 + \sum_{n_\nu=0} z_0^{n_\nu \epsilon_\nu}\right)\right\}, \\ t_0' &= t_0^m \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (21) \end{aligned}$$

where $\omega'_1\,(E)$ is the number of partition of E_1, into sets of $\epsilon_0, \epsilon_1, \ldots \epsilon_\nu, \ldots$ of which no part is equal to ϵ_ν. Then the spectral-distribution of radiation energy becomes

$$\bar{n}_\nu = \frac{A_\nu z_0^{\epsilon_\nu}}{1 - z_0^{\epsilon_\nu}} = \frac{A_\nu}{e^{\epsilon_\nu/kT} - 1}. \qquad \ldots \quad \ldots \quad \ldots \quad (22)$$

Similarly, the microscopic distribution for molecules with respect of energy can be obtained. This is again same as that in the paper I.

Formula for fluctuations can be obtained similarly and similar to these in the previous paper.

Part III. Assembly composed of Matter of Two Different Types

1. *Description of System: Law of Probability-distribution*

The system means certain amount of E and certain amounts M_1 and M_2 of matters of two (chemically) different types, contained in a definite volume in a definite environment. For simplicity, it will be assumed that there is no chemical reaction in the assembly and that the condition of the system and the environment is such that the contribution in the energy due to the free radiation in the system may be taken as insignificantly small and so will be neglected.

Here, as before, a constant a priori z for each unit of energy to occur within the volume under consideration and constant a priori probabilities t_1 and t_2 for unit masses of matter of types (1) and (2) to be in the volume respectively will be introduced. Then, the probability of occurrences of the system to be in a state specified by E, M_1 and M_2 is given by

$$P(t_1, t_2, z, E, M_1, M_2) = \frac{W(E, M_1, M_2)z^E t_1^{M_1} t_2^{M_2}}{\Sigma\Sigma\Sigma\, W(E, M_1, M_2)z^E t_1^{M_1} t_2^{M_2}}$$

$$= \frac{W(E, M_1, M_2)z^E t_1^{M_1} t_2^{M_2}}{f(t_1, t_2, z)}, \quad \ldots \quad \ldots \quad (23)$$

where

$$f(t_1, t_2, z) = \sum_E \sum_{M_1} \sum_{M_2} W(E, M_1, M_2)z^E t_1^{M_1} t_2^{M_2}. \quad \ldots \quad \ldots \quad \ldots \quad (24)$$

The above may be looked upon as same form of Baye's theorem. As before, for determining z, t_1, t_2 for the distribution law, in agreement with usual ideas of statistical equilibrium, the real values of E_0, M_{10}, M_{20} (taken to be known from the observations in the classical sense) are assumed to correspond to the maximum of the probability of occurrence considered as functions of z, t_1, t_2 for fixed values of $E = E_0$, $M_1 = M_{10}$, $M_2 = M_{20}$. Thus, the estimation of parameters z, t_1 and t_2 is similar to that in statistics by principle of maximum likelihood.

2. *Behaviour of Functions of $W(E, M_1, M_2)$, $f(t_1, t_2, z)$, etc.*

All these functions are similar to those in the paper I, and in the parts I and II of this paper, and some similar properties. As in the paper I and the part II of this paper, it can be easily shown that

$$f(t_1, t_2, z) = f_1(t_1, z)f_2(t_2, z), \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (25)$$

where

$$W(E, M_1, M_2) = \sum_{E_1+E_2=E} W_1(E_1, M_1)\, W_2(E_2, M_2), \quad \ldots \quad \ldots \quad (26)$$

$$f_1(t_1, z) = \sum_{E_1} \sum_{M_1} W_1(M_1, E_1)z^{E_1} t^{M_1}, \quad \ldots \quad \ldots \quad \ldots \quad (27)$$

$$f_2(t_2, z) = \sum_{E_2} \sum_{M_2} W_2(M_2, E_2)z^{E_2} t^{M_2}, \quad \ldots \quad \ldots \quad \ldots \quad (28)$$

and

$$E = E_1 + E_2, \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (29)$$

E being the total energy of the system and E_1, E_2 being energies shared by matters of types (1) and (2).

As before,

$$P(t_1, t_2, z) \geqslant 0, \quad .. \quad .. \quad .. \quad .. \quad (30)$$

and for infinite rarefactions, $t_1 = 0$, $t_2 = 0$, $z = 0$,

$$P(t_1, t_2, z) = 0, \quad .. \quad .. \quad .. \quad .. \quad (31)$$

and for infinite condensation, $t_1 = 1$, $t_2 = 1$, $z = 1$,

$$P(t_1, t_2, z) = 0. \quad .. \quad .. \quad .. \quad .. \quad (32)$$

Then, $P(t_1, t_2, z)$ must have at least one maximum uniqueness of maximum can be tested as in the paper I and the part I of this paper.

3. *Influence of Variations of Environments on the System*

As before, in order to take into account of slow changes in environment, the equation of continuity (in average) for energy can be written as

$$\overline{dE} = \sum_i \frac{\overline{\partial E}}{\partial x_i} dx_i + d'Q, \quad .. \quad .. \quad .. \quad .. \quad (33)$$

where x_i's are the parameters involved in the definitions of the environments and

$$\left(-\frac{\overline{\partial E}}{\partial x_i}\right) = -\frac{1}{\left(\log \frac{1}{z_0}\right)} \frac{\partial}{\partial x_i} \{\log f(t_{10}, t_{20}, z_0)\}. \quad .. \quad .. \quad (34)$$

Then,

$$\left(\log \frac{1}{z_0}\right) d'Q = \left(\log \frac{1}{z_0}\right)\left\{\overline{dE} - \sum \frac{\overline{\partial E}}{\partial x_i} dx_i\right\}$$

$$= d\left\{\left(\log \frac{1}{z_0}\right)\bar{E}\right\} + \frac{\partial}{\partial z_0}\{\log f(t_{10}, t_{20}, z_0)\} + \sum_i \frac{\partial}{\partial x_i}\{\log f(t_{10}, t_{20}, z_0)\}$$

$$= d\left\{\left(\log \frac{1}{z_0}\right) E_0 + \log f(t_{10}, t_{20}, z_0) - M_{10} \log t_{10} - M_{20} \log t_{20}\right\}. \quad .. \quad (35)$$

Now, according to the argument advanced in the paper I,

$$z_0 = e^{-\frac{1}{kT}}. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (36)$$

Then, the entropy is given by

$$S = \frac{E}{kT} + \log F(t_{10}, t_{20}, T) - M_{10} \log t_{10} - M_2 \log t_{20}. \quad .. \quad .. \quad (37)$$

4. *Laws of Microscopic Distributions*

Now, as before, for deducing microscopic distributions, the system will be assumed to be composed of N_1 and N_2 numbers of particles, viz. molecules or atoms, where

$$M_1 = N_1 m_1, M_2 = N_2 m_2. \quad .. \quad .. \quad .. \quad (38)$$

If the number of ways, in which a particular $n_{1\nu}$ (number of molecules of type (1)) is realized with energy $\epsilon_{1\nu}$ when the state of system is specified by M_{10}, M_{20}

and E_0, is denoted by $w_1'(E-n_{1\nu}\epsilon_{1\nu}, N_1-n_{1\nu}, N_2)$, then the expected value of $n_{1\nu}$ is given by

$$n_{1\nu} = \frac{\sum_{E=0}^{\infty}\sum_{N_1=0}^{\infty}\sum_{N_2=0}^{\infty}\sum_{n_{1\nu}=0}^{N_1} n_{1\nu}w'(E-n_{1\nu}\epsilon_{1\nu}, N_1-n_{1\nu}, N_2)t_1'^{N_1}t_2'^{N_2}z_0^E}{\sum_{E=0}^{\infty}\sum_{N_1=0}^{\infty}\sum_{N_2=0}^{\infty} W(E, N_1, N_2)t_1'^{N_1}t_2'^{N_2}z_0^E}$$

$$= \frac{\left(\sum_{n_{1\nu}=0}^{\infty} n_{1\nu}t_1'^{n_{1\nu}}z_0^{n_{1\nu}\epsilon_{1\nu}}\right)\left[1+\sum_E\sum_{N_1}\sum_{N_2} w'(E, N_1, N_2)t_1'^{N_1}t_2'^{N_2}z_0^E\right]}{\left(1+\sum_{n_{1\nu}=1}^{\infty} t_1'^{n_{1\nu}}z_0^{n_{1\nu}\epsilon_{1\nu}}\right)\left[1+\sum_E\sum_{N_1}\sum_{N_2} w'(E, N_1, N_2)t_1'^{N_1}t_2'^{N_2}z_0^E\right]}$$

$$= \frac{t_1'\frac{\partial}{\partial t_1}\left(1+\sum_{n_{1\nu}=1}^{\infty} t_1'^{n_{1\nu}}z_0^{n_{1\nu}\epsilon_{1\nu}}\right)}{\left(1+\sum_{n_{1\nu}=0}^{\infty} t_1^{n_{1\nu}}z_0^{n_{1\nu}\epsilon_{1\nu}}\right)}$$

$$= t_1'\frac{\partial}{\partial t_1'}\left\{\log\left(1+\sum_{n_{1\nu}=0}^{\infty} t_1'^{n_{1\nu}}z_0^{n_{1\nu}\epsilon_{1\nu}}\right)\right\}$$

$$= t_1'\frac{\partial}{\partial t_1'}\left\{\log g_\nu(t_1', z_0)\right\}, \qquad (39)$$

where

$$\left.\begin{aligned} t_1' &= t_{10}^{m_1} \\ t_2' &= t_{20}^{m_2} \end{aligned}\right\}. \qquad (40)$$

Similar are the expressions for $n_{2\nu}$.

Thus, usual discussions for microscopic distributions will follow as before. The discussion on fluctuations can also be made and standard existing formulae (Tolman, 1946) can be deduced as in the paper I.

General Concluding Remarks

From the discussions in this paper, it is evident that the extension of the method proposed in the paper I to the general cases, viz. of the multi-component systems containing radiation in absence of chemical reactions, is easy and straightforward. Thus, this method, without losing any of the advantageous characteristics, mentioned in the paper I, is powerful enough to yield the usual formulae in the form as given by Fowler (1936) for general cases. The discussions of crystals and of chemical reactions by this method will be subject-matter of future communications.

ABSTRACT

In this paper, the thermodynamic behaviour of systems of different types, viz. those of black-body radiation, of matter and radiation, and of mixtures, has been investigated by the general statistical method, developed in a paper (Dutta, 1953) previously. Expressions for

thermodynamic functions, microscopic distributions, fluctuations, etc., have been obtained in the form given by Fowler. As in the previous paper (Dutta, 1953), it is seen that for investigations of microscopic properties, the introduction of any assumption about microscopic nature is not at all necessary. This assumption is to be introduced only for discussions of microscopic distributions or the like.

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