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## ON MATHEMATICAL MODELS ON STATISTICAL PHYSICS<sup>1</sup>

by

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### Introduction

The word "model" is a term of common usage. In religion, fine arts, literature, science ( physical, biological and social ) and technology, it is used frequently, in two essentially different senses. In finearts paintings, sculpture are prepared after the model taken as a ideal. In religion, the lives of some great men are presented as models after which the followers of that religion try to shape their lives. In architecture or civil engineering, constructions are made after the model designed earlier. On the other hand, models reflecting certain aspects of objective reality, are studied for its proper understanding. In river physics, models of different rivers are studied. Working of the parts of a human body or complicated machine are explained by models.

In view of the complexity of the systems under consideration in statistical physics, study of models are very much significant in the study of fundamental problems and in the understanding some special notions or mechanisms introduced in the subject<sup>3</sup>. In mathematical study of any problem of practical life, science or technology starts with introduction of a mathematical model. After the development of quantum mechanics, specially after Dirac, scientists and investigators are consciously using mathematical models. So, what is generally meant by a mathematical model and the role it plays in statistical physics is the main aim of this discussion. Here, mathematical models will be classified from different aspects.

### 1. Explanation of the term

It is really very difficult to define a model, being an elementary term, clearly and uniquely. A literal meaning of model is a 'design to be followed' or a 'representation of a designed or an actual object', proportional in all dimensions.

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In general discussions, by scientific models, geometrical or mechanical models are traditionally meant. In mathematical theory of a branch or of a phenomenon of science, the mathematical analysis, specification and solution, in one word, mathematical structure used and the consequences are referred to as mathematical models<sup>21, 22</sup>.

In mathematical models of a theory, the results are derived directly from some unproved basic propositions about the primitive notions. These unproved propositions are generally referred to as axioms and postulates<sup>21</sup>. Hilbert's classic work<sup>1</sup> on foundation of geometry is an example of an axiomatic model of mathematical theory.

## 2. Different classification of models according to their purposes.

Different models are studied for different purposes. Those models suitably used to develop a branch of science and to realise its content and foundation properly are to be called global models for that branch of science. Axiomatic development of geometry (Hilbert<sup>1</sup> and that of thermodynamics by Caratheodory<sup>8</sup> or Giles<sup>7</sup> are good illustrations

of global models. Those models, which are useful for the clarification of the paradoxes or for the proper understanding of some special topics or to solve any special problem of controversy of a branch of science are to be called "local" models. Ehrenfest's<sup>2</sup> dog-flea model, Kac<sup>3</sup> models of rotating discs with colour brushes are examples of local models.

A model is phenomenological, when it is used suitably to study inter relations between the phenomena discussed in a branch of science without bringing basic notions of objects. Usual development is an illustration of this type. But the model is designated as fundamental-theory-based, if those physical phenomena may be directly deduced from some fundamental postulates, stated clearly. In kinetic theory of gases<sup>9</sup> or in the development of General theory of Relativity by Einstein the model used is fundamental-theory-based.

Among the models, associated with the physical theories, two sharp classifications with some reverse basic assumptions are the microscopic and the macroscopic models. In the former one, the bodies under consideration are supposed to be composed of a number of small constituent particles like atoms, molecules etc.

In classical macroscopic physics, models are deterministic. In the kinetic theory of gases and usual development of statistical mechanics, models are indeterministic, in the sense, that they are stochastic.

In the modern approach to statistical mechanics, essentially "stochastic" models, which are related with random variables, their probability distributions and the notions connected with them, are used frequently.

### 3. Emergence of essential statistical models.

In the middle of the last century, after the acceptance of molecular theory, the inapplicability of the usual method of traditional dynamics to obtain the solution of the equations of motion of a very large number of constituent particles forming the system under consideration necessitated a statistic basis for the study of the mechanical problem. Thus came the statistical mechanics

Formulation of the entropy law as an inequality was considered as very uncommon in the development of physical theories. So attempts were made to explain the above from theories of usual mechanics based on basic laws expressed by equalities. Various mathematical models, though based on mechanical considerations mostly, were introduced with a view to interpret that law. Purely, mechanical models were proposed and studied by Clausius<sup>10</sup>, Boltzmann<sup>9</sup> Thomson. Mechanical models with statistieal approach to some extent were formulated by Boltzmann (1927) and further developed by Lorentz, Planck<sup>4</sup>, Einstein, Debye, Bose, Fermi<sup>5</sup> and also by Gibbs<sup>11</sup> and by Darwin<sup>12</sup> and Fowles<sup>12</sup> (1927). Other than Gibbs' all these models are microscopic.

Side by side global deterministic, fundamental-theory-based macroscopic models were proposed and developed by Caratheodory<sup>6</sup> (1909) and Giles<sup>7</sup> (1964).

Szilard<sup>8</sup> established that the observed values of every thermodynamic variable should be introduced along with its probability distribution even in macroscopic phenomenological development.

An essentially stochastic, global fundamental models, with macroscopic approach wauffirst proposed and formulated by Dutta<sup>13-17</sup> and Jaynes<sup>18,19</sup> independently. Of course, the inter-relation, better equivalence of the two models are desceis'd by Dutta.

Some local expository models like Ehrenfest's Dog-flea model, Ring-model due to Kac<sup>3</sup> are interesting and useful in the study of irreversible processes.

#### Concluding remarks.

In the development of science, various types of models with specific characteristics are so far proposed and developed to study different natural phenocmena. This is still developing.

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## Study of non-equilibrium thermodynamics by an essentially stochastic model

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**Abstract :** An essentially stochastic model has been developed by Dutta mainly for the study of equilibrium processes. In this paper the same model is used for the study of some problems of non-equilibrium processes as well as it is used here for the deduction of Onsager's relations in a simple and direct manner. Expressions for fluctuations are obtained very simply in this connections.

### 1. Introduction

Amongst different approaches to the statistical foundation of thermodynamics during the last century, almost all were based on mechanical models though latter statistical notions and methods were used to supplement the mechanical reasonings. Some of the approaches involve the notion of microscopic reversibility (Kirkwood and Rice 1959).

Dutta (1953, 1956, 1960, 1965, 1966, 1967) developed a theory based on an essentially statistical approach to investigate the thermodynamic behaviour of a system in equilibrium state. Chakravorty (1970, 1971, 1972, 1973) has also developed this theory further.

An information theoretic approach to statistical thermodynamics was proposed by Jaynes in 1957 and developed further by himself (1965), Schlögl (1966, '67), Ingarden and Urbanik (1962) and Chakravarty (1973). They approached by taking Shannon's (1948) entropy as the general measure of statistical uncertainty and the specification and estimation were made by the method of maximum entropy estimation. In 1968, Dutta proved the equivalence between this method and the method used by himself in his theory.

In this present paper, the problems of non-equilibrium processes have been

studied by using the same stochastic model. By its use Onsager's (1931) relations are deduced in a very simple and direct manner. Also the expressions for fluctuations are obtained very simply.

## 2. Formulation of probability distribution for a thermodynamic system in equilibrium state

In the theory, proposed by Dutta (1953), some fundamental entities which are measurable and additive in nature, specify the instantaneous state of an open thermodynamic system under consideration, to which they belong. This may be considered as a random process. The probability of occurrence of a system with instantaneous values  $M$  and  $E$ , say, the two fundamental entities, may be taken as

$$p(t, z ; M, E) = \frac{t^M z^E}{\sum_M \sum_E t^M z^E} = \frac{t^M z^E}{f(t, z)} \quad (2.1)$$

The statistical parameters  $t, z$  in (2.1) are the apriori probabilities of occurrences of unit quantities of the fundamental entities  $M, E$  in the system respectively and they are to be estimated by a principle, similar to that of maximum likelihood (Dutta 1953 and 1956). The summation in (2.1) is over the different possible values of  $M$  and  $E$  defining different thermodynamically recognisable states of the system. As the summation is taken for all values of  $M$  and  $E$ , so  $f(t, z)$  does not depend  $M$  and  $E$ .

The law of distribution estimated is

$$p(t_0, z_0 ; M, E) = \frac{t_0^M z_0^E}{f(t_0, z_0)} \quad (2.2)$$

where  $t_0, z_0$  are given by

$$M_0 = t_0 \frac{\partial}{\partial t_0} \log f(t_0, z_0) \quad (2.3)$$

$$E_0 = z_0 \frac{\partial}{\partial z_0} \log f(t_0, z_0) \quad (2.4)$$

## 3. Identification with physical quantities

If one identifies  $M$  and  $E$  with mass and energy, then entropy can be obtained from the equation of energy conservation as well as from that of mass conservation. By usual method, in the former case, the integrating factor can be associated with temperature, in the latter case, the integrating factor can be

associated with chemical potential. Not only that the increasing property of the entropy can also be proved (Dutta 1953), these equations are

$$z_0 = e^{-\frac{1}{kT}} \quad (3.1)$$

$$S = -\log \frac{t_0 \bar{M} z_0 \bar{E}}{f(t_0, z_0)} \quad (3.2)$$

$$t_0 = e^{\frac{\mu}{kT}} \quad (3.3)$$

#### 4. Generalisation to non-equilibrium thermodynamics

The probability distribution of a thermodynamic system in equilibrium state, under prescribed conditions may as well be expressed in exponential form. It may also be considered as the probability at the time  $t=0$ , viz

$$P(x, 0) = \frac{e^{\alpha x}}{\phi(\alpha)} \quad \text{where } \phi(\alpha) = \int e^{\alpha x} dx \quad (4.1)$$

$$P(x, y, 0) = \frac{e^{\alpha x + \beta y}}{\phi(\alpha, \beta)} \quad \text{where } \phi(\alpha, \beta) = \iint e^{\alpha x + \beta y} dx dy \quad (4.2)$$

$$P(x_1, x_2, \dots, x_n, 0) = \frac{e^{\sum_{i=1}^n \alpha_i x_i}}{\phi(\alpha_1, \alpha_2, \dots, \alpha_n)}, \quad \phi(\alpha_1, \alpha_2, \dots, \alpha_n) = \int \dots \int e^{\sum_{i=1}^n \alpha_i x_i} d\tau$$

$$d\tau = dx_1 dx_2 \dots dx_n \quad (4.3)$$

according as the basic entity is a single one or more than that.  $\alpha_i$ 's are the statistical parameters but may be associated with physical quantities (Sec. 3).

It is assumed that in non-equilibrium state very near to equilibrium all the above methods of estimation of probability distribution and also the interpretation of the parameters are valid. The process is supposed to occur so slowly that at every instant the system may be supposed to be in equilibrium. Hence the form of the probability distribution for equilibrium state may be used to obtain the probability distribution near the instant  $t$ , which is as follows :

$$P(x, t) = \frac{e^{\alpha(t)x}}{\phi(\alpha(t))} \quad \text{where } \phi(\alpha(t)) = \int e^{\alpha(t)x} dx \quad (4.4)$$

$$P(x, y, t) = \frac{e^{\alpha(t)x + \beta(t)y}}{\phi(\alpha(t), \beta(t))} \quad \text{where } \phi(\alpha(t), \beta(t)) = \iint e^{\alpha(t)x + \beta(t)y} dx dy \quad (4.5)$$

$$P(x_1, x_2, \dots, x_n, t) = \frac{e^{\sum_{i=1}^n \alpha_i(t)x_i}}{\phi(\alpha_1(t), \dots, \alpha_n(t))}$$

$$\text{where } \phi(\alpha_1(t), \alpha_2(t) \dots \alpha_n(t)) = \int \dots \int e^{\sum_{i=1}^n \alpha_i(t) x_i} d\tau; \quad d\tau = dx_1 dx_2 \dots dx_n \quad (4.6)$$

with usual interpretation of  $\alpha$ 's. In this formulation of probability distribution, the parameters  $\alpha_i$ 's are assumed to be time-dependent whereas the  $x_i$ 's are mere random variables. Continuous variables are used as the process is supposed to occur very slowly.

### 5. Onsager's reciprocal relation

Onsager's reciprocal relation is considered as a fundamental law in the linear theory of irreversible phenomena. Starting from the time-dependent probability distribution, which is developed in Sec. 4, we may arrive at the Onsager's reciprocal relation, by very simple mathematics. Here also, the differences or the gradients of some thermodynamic quantities which are in general intensive variables like temperature, concentration, some potentials etc. are considered as the thermodynamic generalised forces.

If  $x, y$  be the two basic entities of a thermodynamic system satisfying the assumptions of additivity and conservation together with, the occurrence of the non-equilibrium state is very slow and very near to equilibrium state, then

$$\bar{x}(t) = x_o(t) = \frac{\iint x e^{\alpha(t)x + \beta(t)y} dx dy}{\phi(\alpha(t), \beta(t))} \quad (5.1)$$

$$\bar{y}(t) = y_o(t) = \frac{\iint y e^{\alpha(t)x + \beta(t)y} dx dy}{\phi(\alpha(t), \beta(t))} \quad (5.2)$$

Now,

$$\Delta\phi = \phi_\alpha \Delta\alpha + \phi_\beta \Delta\beta = \Delta\alpha \iint x e^{\alpha(t)x + \beta(t)y} dx dy + \Delta\beta \iint y e^{\alpha(t)x + \beta(t)y} dx dy \quad (5.3)$$

where

$$\begin{aligned} \phi &= \iint e^{\alpha(t)x + \beta(t)y} dx dy \\ \frac{\Delta\phi}{\phi} &= \Delta\alpha x_o(t) + \Delta\beta y_o(t) \end{aligned} \quad (5.4)$$

again from (5.1)

$$\begin{aligned} \Delta x_o &= \frac{\partial x_o}{\partial \alpha} \Delta\alpha + \frac{\partial x_o}{\partial \beta} \Delta\beta \\ &= \frac{1}{\phi^2} [\phi \iint x^2 e^{\alpha(t)x + \beta(t)y} dx dy - \phi_\alpha \iint x e^{\alpha(t)x + \beta(t)y} dx dy] \Delta\alpha \\ &\quad + \frac{1}{\phi^2} [\phi \iint x y e^{\alpha(t)x + \beta(t)y} dx dy - \phi_\beta \iint x e^{\alpha(t)x + \beta(t)y} dx dy] \Delta\beta \\ &= [\bar{x}^2 - (\bar{x})^2] \Delta\alpha + [\iint (xy - x_o y_o) P(x, y, t) dx dy] \Delta\beta \end{aligned}$$

then we may write

$$\frac{dx_o}{dt} = [\bar{x}^2 - (\bar{x})^2] \frac{d\alpha}{dt} + [\iint (xy - x_o y_o) P(x, y, t) dx dy] \frac{d\beta}{dt} \quad (5.5)$$

Similarly, it can be proved

$$\frac{dy_o}{dt} = [\iint (xy - x_o y_o) P(x, y, t) dx dy] \frac{d\alpha}{dt} + [\bar{y}^2 - (\bar{y})^2] \frac{d\beta}{dt} \quad (5.6)$$

Let us denote

$$\left. \begin{aligned} \frac{dx_o}{dt} &= J_1 & \dot{\alpha} \left( = \frac{d\alpha}{dt} \right) &= x_1 \\ \frac{dy_o}{dt} &= J_2 & \dot{\beta} \left( = \frac{d\beta}{dt} \right) &= x_2 \end{aligned} \right\} \quad (5.6a)$$

The  $J$ 's and  $X$ 's are commonly used to denote the thermodynamic fluxes and forces respectively as also used by Dutta (1967). Then from (5.5), (5.6)

$$\left. \begin{aligned} J_1 &= a_{11}x_1 + a_{12}x_2 \\ J_2 &= a_{21}x_1 + a_{22}x_2 \end{aligned} \right\} \quad (5.7)$$

$$\text{where } a_{12} = a_{21} = \iint (xy - x_o y_o) P(x, y, t) dx dy \quad (5.8)$$

which proves Onsager's reciprocal relation.  $\alpha, \beta$ , when taken as thermodynamic forces, need a bit explanation. It is already interpreted as to how the statistical parameters are identified with thermodynamic quantities (Dutta, 1953, Sec 3). It may be explained more clearly by taking a concrete example. If the two basic entities  $X, Y$  stand for energy and mass of a thermodynamic system respectively, then the parameters  $\alpha$  and  $\beta$  are associated with temperature and chemical potential respectively, which are, no doubt, intensive thermodynamic variables and hence  $\alpha, \beta$ , may without any confusion, be treated as thermodynamic forces causing the fluxes viz. heat flow  $\frac{dx_o}{dt}$  and mass flow  $\frac{dy_o}{dt}$ .

## 6. The most general case

Assuming that there exist  $n$  basic entities in the thermodynamic system and following the similar procedure, starting from the probability distribution given in (4.6), Onsager's Reciprocal Relation may be established.

$$\bar{x}_i = \frac{\int \dots \int x_i e^{\sum \alpha_i(t) x_i} d\tau}{\phi(\alpha_1(t), \dots, \alpha_n(t))} \quad (6.1)$$

$$\dot{\phi} = \frac{d\phi}{dt} = \sum_{i=1}^n \frac{\partial \phi}{\partial \alpha_i} \dot{\alpha}_i = \sum (\int \dots \int x_i e^{\sum \alpha_i(t) x_i} d\tau) \dot{\alpha}_i \quad (6.2)$$

$$\frac{\dot{\phi}}{\phi} = \sum_{i=1}^n \bar{x}_i \dot{\alpha}_i \quad (6.3)$$

$$\begin{aligned} \frac{\partial \bar{x}_i}{\partial t} &= \frac{1}{\phi^2} \left[ \phi \left\{ \dot{\alpha}_i \int x_i^2 e^{\sum \alpha_i(t) x_i} d\tau + \sum_{\substack{k=1 \\ k \neq i}}^n \dot{\alpha}_k \int x_i x_k e^{\sum \alpha_i(t) x_i} d\tau \right\} \right. \\ &\quad \left. - \dot{\phi} \int x_i e^{\sum \alpha_i(t) x_i} d\tau \right] \\ &= \frac{1}{\phi} \left[ \dot{\alpha}_i \int x_i^2 e^{\sum \alpha_i(t) x_i} d\tau + \sum_{\substack{k=1 \\ k \neq i}}^n \dot{\alpha}_k \int x_i x_k e^{\sum \alpha_i(t) x_i} d\tau \right. \\ &\quad \left. - \sum_{j=1}^n \dot{\alpha}_j \bar{x}_j \int x_i e^{\sum \alpha_i(t) x_i} d\tau \right] \\ &= \dot{\alpha}_i \left[ \int x_i^2 p d\tau - (\int x_i p d\tau)^2 \right] + \sum_{\substack{k=1 \\ k \neq i}}^n \dot{\alpha}_k \int (x_i x_k - \bar{x}_i \bar{x}_k) p d\tau \end{aligned}$$

where  $p$  stands for  $p(x_1, x_2, \dots, x_n, t)$  and single integral actually stands for  $n$ -integral.

$$\begin{aligned} \frac{\partial \bar{x}_i}{\partial t} &= [\bar{x}_i^2 - (\bar{x}_i)^2] \dot{\alpha}_i + \sum_{\substack{k=1 \\ k \neq i}}^n \dot{\alpha}_k \int (x_i x_k - \bar{x}_i \bar{x}_k) p d\tau \\ &\quad i=1, 2, \dots, n \end{aligned} \tag{6.4}$$

This result may be written in matrix form

$$J = [a_{ij}] X \tag{6.5}$$

where

$$J = \begin{bmatrix} \frac{\partial \bar{x}_1}{\partial t} \\ \vdots \\ \frac{\partial \bar{x}_n}{\partial t} \end{bmatrix} \quad X = \begin{bmatrix} \dot{\alpha}_1 \\ \dot{\alpha}_2 \\ \vdots \\ \dot{\alpha}_n \end{bmatrix} \tag{6.6}$$

$[a_{ij}]$  is a  $n \times n$  matrix, of which

$$\left. \begin{aligned} a_{ii} &= [\bar{x}_i^2 - (\bar{x}_i)^2] \\ a_{ij} &= \int (x_i x_j - \bar{x}_i \bar{x}_j) p d\tau \\ a_{ji} &= \int (x_j x_i - \bar{x}_j \bar{x}_i) p d\tau \end{aligned} \right\} \tag{6.7}$$

Hence

$$a_{ij} = a_{ji}$$

i.e.  $[a_{ij}]$  is a symmetric matrix.

$$\tag{6.3}$$

Thus the Onsager reciprocal relation is established by such a simple way. The extra advantage in this development is that, not only that important relation, the Onsager relation

$$J_i = \sum_{j=1}^n a_{ij} x_j \quad i=1, 2, \dots, n$$

in which  $a_{ij} = a_{ji}$

is established, but also, the expressions for the co-efficients  $a_{ij}$ ,  $i=1, \dots, n$ ,  $j=1, \dots, n$  are obtained.  $a_{ii}$  is associated with the fluctuation of  $i^{\text{th}}$  entity and  $a_{ij}$  is associated with the co-relation co-efficient between the  $i^{\text{th}}$  and  $j^{\text{th}}$  entities.

### 7. Expression for fluctuation in energy

Let us consider a thermodynamic system in which energy is the only single basic entity. The whole system is in contact with a heat bath so that transfer of energy between the system and the environment is permissible, i.e. the system is supposed to be an open one. In addition to the fundamental assumptions of additivity and conservation, we assume that the change of energy, very near to equilibrium state occurs very slowly and steadily, so that the energy at the time  $t$  in the system may be given by the equation

$$x_o(t) = x_o(o) + \gamma t \quad (7.1)$$

where  $x_o(t)$  = observed value of the energy in the system at the instant  $t$ .

$x_o(o)$  = observed value of the energy in the system at  $t=0$  i.e. in the equilibrium state at the start.

From (5.1)

$$\bar{x}(t) = x_o(t) = \frac{\int x e^{\alpha(t)x} dx}{\phi(\alpha(t))} \quad (7.2)$$

Now

$$\frac{\dot{\phi}(\alpha(t))}{\phi(\alpha(t))} = \frac{\phi_\alpha(\alpha(t)) \dot{\alpha}(t)}{\phi(\alpha(t))} = \dot{\alpha}(t) x_o(t) \quad (7.3)$$

where the dot denotes the differentiation with respect to  $t$ . For an infinitesimal change in energy, from (7.1)

$$\gamma = \frac{\partial x_o}{\partial t} \quad (7.4)$$

$$= \dot{\alpha}(t) [\bar{x}^2 - (\bar{x})^2] \quad (7.5)$$

as

$$\frac{\partial x_o}{\partial t} = \frac{\phi(\alpha(t)) [\dot{\alpha}(t) \int x^2 e^{\alpha(t)x} dx] - \dot{\phi}(\alpha(t)) \int x e^{\alpha(t)x} dx}{[\phi(\alpha(t))]^2}$$

$$= \dot{\alpha}(t) [\bar{x}^2 - (\bar{x})^2] \text{ by (7.2) and (7.3)}$$

Now by (7.4) and (7.5)

$$\begin{aligned} \text{Var}(x) &= \bar{x}^2 - (\bar{x})^2 \\ &= \frac{\gamma}{\dot{\alpha}(t)} \\ &= \frac{\frac{\partial x_o}{\partial T} \frac{dT}{dt}}{\frac{1}{kT^2} \frac{dT}{dt}} = kT^2 C_v \end{aligned} \quad (7.6)$$

where  $C_v$  is the specific heat at constant volume

$$\text{and } \alpha = -\frac{1}{kT}$$

Thus we obtain a standard and very important result of fluctuation of energy by such a simple mathematical method.

The fluctuation of other basic entities viz  $\text{Var}(y)$  may be obtained by similar method.

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