

CHAPTER - II

DUTTA'S STOCHASTIC MODEL AND
IRREVERSIBILITY

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2.1 INTRODUCTION

In this chapter, we shall describe Dutta's essentially stochastic model formulated for the equilibrium state of a thermodynamic system and then discuss, how this same model with the same structure with slight modification may be used successfully to study the irreversible phenomena too.

2.2 DUTTA'S STOCHASTIC MODEL FOR EQUILIBRIUM STATE

2.2.1 Background

The extensive thermodynamic quantities involved in the phenomenological experiments are measured by their average values. But these measured values are never exactly the same with the average values. They deviate more or less from the average values. This type of deviations regarding the relevant physical quantities from the corresponding averages take an important part in some finer experiments like light scattering, torsional oscillation of mirror suspended in high vacuum etc. These facts supports the introduction of an essentially probabilistic approach in macroscopic physics. The occurrence of a thermodynamic system in a

definite state may be considered as a random event due to the fact that the instantaneous state of the system caused due to the transfer of the basic entities between the environment and the system, changes with time. This is the basis of the approach leading to the essentially stochastic model.

2.2.2 Fundamental Entities and Basic Assumptions

The two fundamental entities with which Dutta started his essentially stochastic theory (1951, '53, '56, '59, '66, '72, '78) are those quantities which are actually measurable in an experiment. These entities, denoted by M and E , are supposed to be additive in nature and are supposed to satisfy the conservation law. The system under consideration is taken to be open, which means free transfer of these basic entities between the system and the environment is admitted, resulting to the change in the instantaneous state of the system, specified by the basic entities. This may be considered as a random process so that the existence of the probability distribution corresponding to the instantaneous state of the system indicated by the instantaneous values of M and E is quite justified.

2.2.3 Formulation of Probability Distribution

The probability of occurrence of a system in a state with instantaneous values of M and E of the two fundamental

entities may be taken as

$$p(t,z ; M,E) = \frac{t^M z^E}{\sum' \sum' t^M z^E} = \frac{t^M z^E}{f(t,z)}, \quad \dots(2.1)$$

where t, z are a priori probabilities of occurrence of unit quantities of the fundamental entities M and E in the system respectively. The summation $\sum' \sum'$ are to be extended over all values of M and E and terms are repeated in the summation, if there be a number of states corresponding to a particular set of values for M and E . If $W(M,E)$ be such a number, then the probability of occurrence of the system is

$$P(t,z ; M,E) = \frac{W(M,E) t^M z^E}{f(t,z)}, \quad \dots(2.2)$$

where

$$f(t,z) = \sum' \sum' t^M z^E = \sum \sum W(M,E) t^M z^E, \quad \dots(2.3)$$

where the latter summation extends over all values of M and E .

Evidently

$$W(M,E) \geq 0 \quad \dots(2.4)$$

If the system (M,E) consists of two subsystems with the basic entities (M_1, E_1) and (M_2, E_2) , so that

$$M = M_1 + M_2 \quad \dots(2.5)$$

$$E = E_1 + E_2 \quad \dots(2.6)$$

then

$$W(M,E) = \sum_{\substack{M_1+M_2=M \\ E_1+E_2=E}} W(M_1, E_1) W(M_2, E_2) , \quad \dots(2.7)$$

where the summation extends over all values of $M_1, M_2 ; E_1, E_2$ with the constraints (2.5) and (2.6). It may easily be proved that $f(t,z)$ is multiplicative.

$$\begin{aligned} f(t,z) &= \sum \sum W(M,E) t^M z^E \\ &= \sum \sum \sum W(M_1, E_1) W(M_2, E_2) t^{M_1+M_2} z^{E_1+E_2} \\ &= \sum \sum W(M_1, E_1) t^{M_1} z^{E_1} \sum \sum W(M_2, E_2) t^{M_2} z^{E_2} \\ &= f_1(t,z) f_2(t,z) \quad \dots(2.8) \end{aligned}$$

The parameter t, z , in the probability distribution (2.1) are estimated by using a principle similar to that of maximum likelihood following the comments of Doob (1953), viz., the actually observable values are the most probable values. Thus to obtain the correct distribution law, t, z , should be such that the expression for the probability distribution (2.1) will be the

maximum at the observed values M_0, E_0 , i.e., the correct law of distribution of state is

$$p(t_0, z_0; M, E) = \frac{t_0^M z_0^E}{f(t_0, z_0)}, \quad \dots(2.9)$$

where t_0, z_0 , are given by

$$M_0 = t_0 \frac{\delta}{\delta t_0} \log f(t_0, z_0) \quad \dots(2.10)$$

$$E_0 = z_0 \frac{\delta}{\delta z_0} \log f(t_0, z_0) \quad \dots(2.11)$$

A very simple calculation shows that the average values of M and E are equal to M_0 and E_0 respectively,

$$\begin{aligned} \bar{M} &= \frac{\sum \sum M W(M, E) t_0^M z_0^E}{\sum \sum W(M, E) t_0^M z_0^E} \\ &= t_0 \frac{\delta}{\delta t_0} \left\{ \log f(t_0, z_0) \right\} = M_0 \quad \dots(2.12) \end{aligned}$$

It may be noted that the distribution is symmetrical about mode.

2.2.4 Identification of the Physical Quantities

Let x_1 be a finite number of external parameters specifying a definite environment, in which the system is supposed

to exist. The different instantaneous state of the system is affected due to the infinitesimal variations in these parameters.

Assuming the conservation for E , we can write

$$dE = \sum_i \frac{\delta E}{\delta x_i} dx_i + d'q \quad \dots(2.13)$$

The co-efficients $\frac{\delta E}{\delta x_i}$ determine the increase of E in the system caused by the change of x_i and $d'q$ is the increase of E due to its flow from outside and other similar processes and this is not considered in the first term.

Since only the average properties are of real physical significance and which one is the initial state can not be determined, we write

$$d\bar{E} = \sum \left(\frac{\delta \bar{E}}{\delta x_i} \right) dx_i + d'Q \quad , \quad \dots(2.14)$$

where $d'Q$ stands for the average value of $d'q$. Now

$$- \left(\frac{\delta \bar{E}}{\delta x_1} \right) = \left(\frac{1}{\log \frac{1}{z_0}} \right) \frac{\delta}{\delta x_1} \left\{ \log f(t_0, z_0) \right\} \quad \dots(2.15)$$

so that

$$\left(\log \frac{1}{z_0} \right) d'Q = d \left\{ - \log \frac{t_0^{\bar{M}} z_0^{\bar{E}}}{f(t_0, z_0)} \right\} \quad \dots(2.16)$$

In the same way, assuming the conservation for the other fundamental entity M ,

$$d \bar{M} = \Sigma \frac{\delta \bar{M}}{\delta x_1} dx_1 + d'P \quad \dots(2.17)$$

Now,

$$- \left(\frac{\delta \bar{M}}{\delta x_1} \right) = \left(\frac{1}{\log \frac{1}{t_0}} \right) \frac{\delta}{\delta x_1} \left\{ \log f(t_0, z_0) \right\}, \dots(2.18)$$

so that

$$\left(\log \frac{1}{t_0} \right) d'P = d \left\{ - \log \frac{t_0^{\bar{M}} z_0^{\bar{E}}}{f(t_0, z_0)} \right\}, \quad \dots(2.19)$$

where $d'P$ is the average value of $d'p$, the term denoting the flow of the entity M .

For the physical interpretation, if one identifies M and E with mass and energy and the equation (2.13) with the first law of thermodynamics, one gets

$$\frac{1}{kT} = \log \left(-\frac{1}{z_0} \right) \quad \dots(2.20)$$

$$S = - \log \frac{t_0^{\bar{M}} z_0^{\bar{E}}}{f(t_0, z_0)} \quad \dots(2.21)$$

$$\frac{\mu}{kT} = \log t_0, \quad \dots(2.22)$$

where k is the Boltzmann constant, S, T, μ are the entropy, temperature and the chemical potential respectively. The function $f(t, z)$ is the partition function which satisfies the multiplicative law, viz.

$$f(t, z) = f_1(t, z) \cdot f_2(t, z) ,$$

for the two part systems separated by (geometrical) partition without disturbing the system.

From the above discussion, the important inference is that the entropy may be obtained easily from the equation of energy conservation as well as from the equation of mass conservation.

In the former case, temperature is associated with the integrating factor, whereas in the latter case, chemical potential is connected with the integrating factor. Identifying the equation (2.14) with the first law of thermodynamics, $-\sum \frac{\delta \bar{E}}{\delta x_1}$ can be easily obtained as external work done by the system. Thus if the generalised forces in the system is taken as X_1 , then $X_1 = \frac{\delta \bar{E}}{\delta x_1}$.

In this approach one should distinguish between the fundamental and non-fundamental entities. Only the fundamental entity should be considered. The conservation law for each fundamental entity leads to the expression of entropy but to different

conjugate potentials viz., temperature, chemical potentials etc. Besides mass and energy, charge, momentum, spin etc. may also be considered as fundamental entities.

2.2.5 Expression for Entropy

The expression for the entropy S given by (2.21) can be reduced to the following form (Dutta 1965).

$$\begin{aligned}
 S &= k \left\{ \log f(t_0, z_0) - \bar{M} \log t_0 - \bar{E} \log z_0 \right\} \\
 &= k \left\{ \log f(t_0, z_0) \sum' \sum' p(t_0, z_0 ; M, E) \right. \\
 &\quad \left. - \log t_0 \sum' \sum' M p(t_0, z_0 ; M, E) - \log z_0 \sum' \sum' E p(t_0, z_0 ; M, E) \right\} \\
 &= -k \sum' \sum' p(t_0, z_0 ; M, E) \log p(t_0, z_0 ; M, E) \quad \dots (2.23)
 \end{aligned}$$

The increasing property of the entropy S under certain circumstances can easily be proved.

Let us consider two isolated similar systems with the fundamental entities (M_1, E_1) and (M_2, E_2) and let (t'_0, z'_0) , (t''_0, z''_0) be the estimated values of the parameters in the respective system. Let us denote

$$S_1(t, z) = -k \log \frac{t^{M_1} z^{E_1}}{f_1(t, z)} = -k \log p(t, z; M_1, E_1) \quad \dots (2.24)$$

$$S_2(t, z) = -k \log \frac{t^{M_2} z^{E_2}}{f_2(t, z)} = -k \log p(t, z; M_2, E_2) \quad \dots(2.25)$$

Obviously $p(t, z; M_1, E_1)$ and $p(t, z; M_2, E_2)$ are maximum for (t'_0, z'_0) and (t''_0, z''_0) respectively.

Obviously

$$S_1(t, z) \geq S_1(t'_0, z'_0) \quad \dots(2.26)$$

$$S_2(t, z) \geq S_2(t''_0, z''_0) \quad \dots(2.27)$$

Now,

$$\begin{aligned} S(t_0, z_0) &= -k \log p(t_0, z_0; M, E) \\ &= -k \log \frac{t_0^M z_0^E}{f(t_0, z_0)} \\ &= -k \log \left(\frac{t_0^{M_1} z_0^{E_1}}{f_1(t_0, z_0)} \cdot \frac{t_0^{M_2} z_0^{E_2}}{f_2(t_0, z_0)} \right) \\ &= S_1(t_0, z_0) + S_2(t_0, z_0) \quad \dots(2.28) \end{aligned}$$

Then from (2.26) and (2.27)

$$S(t_0, z_0) \geq S_1(t'_0, z'_0) + S_2(t''_0, z''_0) \quad \dots(2.29)$$

In thermodynamics, this coupling is associated with diffusion, mixing, conduction etc., and so the entropy of coupled systems (isolated) increases.

2.2.6 Fluctuation

When the probability distribution for M and E is known, it is possible to obtain the fluctuation of M and E as follows,

$$\overline{E^2} = \frac{\sum \sum E^2 W(M,E) t_0^M z_0^E}{\sum \sum W(M,E) t_0^M z_0^E} = z_0 \left(-\frac{\delta \bar{E}}{\delta z_0} \right) + (\bar{E})^2 \dots (2.30)$$

so that,

$$\text{Var}(E) = \overline{(E - \bar{E})^2} = z_0 \frac{\delta \bar{E}}{\delta z_0} \dots (2.31)$$

Similarly,

$$\text{Var}(M) = \overline{(M - \bar{M})^2} = t_0 \frac{\delta \bar{M}}{\delta t_0} \dots (2.32)$$

It can be shown that,

$$\text{Cov}(M,E) = \overline{(M - \bar{M})(E - \bar{E})} = t_0 \frac{\delta \bar{E}}{\delta t_0} = z_0 \frac{\delta \bar{M}}{\delta z_0} \dots (2.33)$$

For fixed observed values of M and E , the distribution for t, z can be proved Gaussian. For this purpose, we write the

distribution in exponential form in the following manner.

$$p(t, z; M_0, E_0) = \frac{t^{M_0} z^{E_0}}{f(t, z)} = g(t, z; M_0, E_0) = e^{G(t, z)} \dots (2.34)$$

By Taylor's expansion of $G(t, z)$ about (t_0, z_0) which is the set of values of (t, z) estimated from likelihood equations, we get,

$$\begin{aligned} G(t, z) &= G(t_0, z_0) + \frac{1}{2} (t - t_0)^2 \left(\frac{\delta^2 G}{\delta t^2} \right)_0 \\ &\quad + 2(t - t_0)(z - z_0) \left(\frac{\delta^2 G}{\delta t \delta z} \right)_0 + \frac{1}{2} (z - z_0)^2 \left(\frac{\delta^2 G}{\delta z^2} \right)_0 \\ &\quad + \text{terms containing higher powers of } (t - t_0) \\ &\quad \text{and } (z - z_0) \dots (2.35) \end{aligned}$$

Hence,

$$p(t, z; M_0, E_0) = \text{Constant} \cdot \frac{t_0^{M_0} z_0^{E_0}}{f(t_0, z_0)} \exp \left[- \frac{1}{2} (t - t_0)^2 \left(\frac{\delta^2 G}{\delta t^2} \right) + \dots \right] \dots (2.36)$$

The constant is determined from the condition of normalisation and the form of the distribution is Gaussian.

Knowing the distribution of t, z it is possible to find the fluctuation of t and z , by using well-known results of

statistics (Dutta, 1966).

$$\text{Var}(t) = \frac{1}{\text{Var}(M) \cdot \Delta} \quad \dots(2.37)$$

$$\text{Var}(z) = \frac{z_0^2}{\text{Var}(E) \cdot \Delta} \quad \dots(2.38)$$

$$\text{Cov}(t, z) = \frac{t_0 z_0}{\text{Cov}(M, E) \cdot \Delta} \quad \dots(2.39)$$

$$= \frac{t_0 z_0}{\{\text{Var}(E) \text{Var}(M)\}^{1/2} \cdot \Delta} \quad \dots(2.40)$$

where $\Delta = 1 - \gamma_{M,E}^2$, $\gamma_{M,E}$ being the correlation between t and z is given by

$$\gamma_{t,z} = \frac{\text{Cov}(t, z)}{\text{Var}(t) \text{Var}(z)^{1/2}} = \gamma_{M,E} \quad \dots(2.41)$$

Putting

$$z_0 = e^{-\frac{1}{kT}}, \quad t_0 = e^{\frac{\mu}{kT}},$$

the fluctuation of temperature is obtained (Dutta, 1966).

$$\begin{aligned} \text{Var}(T) &= \left(-\frac{\delta T}{\delta z_0} \right)^2 \text{Var}(z_0) \\ &= \frac{kT^2}{C_v} (1 - \gamma_{M,E}^2)^{-1}, \quad \dots(2.42) \end{aligned}$$

where C_v is the specific heat at constant volume.

This expression for fluctuation in temperature obtained by Dutta (1966) differs from that obtained by Landau and Lifshitz (1958) by the multiplicative factor $(1 - \gamma_{M,E}^2)^{-1}$. This becomes identical when $\gamma_{M,E} = 0$. Chakrabarti (1971) derived the same result from different point of view.

2.3 GENERALISATION TO NON-EQUILIBRIUM THERMODYNAMICS

The probability distribution, so far discussed, for the equilibrium state of a thermodynamic system, satisfying certain basic assumptions, may as well be expressed in exponential form. It may also be considered as the probability at the time $t = 0$, viz. , .

$$P(x,0) = \frac{e^{\alpha x}}{\phi(\alpha)} , \text{ where } \phi(\alpha) = \int e^{\alpha x} dx \quad \dots(2.43)$$

$$P(x,y,0) = \frac{e^{\alpha x + \beta y}}{\phi(\alpha, \beta)} , \text{ where } \phi(\alpha, \beta) = \int \int e^{\alpha x + \beta y} dx dy \quad \dots(2.44)$$

$$P(x_1, x_2, \dots, x_n, 0) = \frac{e^{\sum_{i=1}^n \alpha_i x_i}}{\phi(\alpha_1, \alpha_2, \dots, \alpha_n)} , \quad \dots(2.45)$$

$$\text{where } \phi(\alpha_1, \dots, \alpha_n) = \int \dots \int e^{\sum_{i=1}^n \alpha_i x_i} d\zeta ,$$

$$d\zeta = dx_1 dx_2 \dots dx_n ,$$

according as the basic entity is a single one or more than that; α_1 's are the statistical parameters, but may be associated with physical quantities.

This method of deriving the probability distribution can be easily generalised to obtain the probability distribution of a non-equilibrium state of the system very near to equilibrium. It is assumed that in the 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 at the instant t , which is as follows

$$P(x,t) = \frac{e^{\alpha(t)x}}{\phi(\alpha(t))}, \text{ where } \phi(\alpha(t)) = \int e^{\alpha(t)x} dx \dots(2.46)$$

$$P(x,y,t) = \frac{e^{\alpha(t)x+\beta(t)y}}{\phi(\alpha(t), \beta(t))}, \text{ where } \phi(\alpha(t), \beta(t)) = \iint e^{\alpha(t)x+\beta(t)y} dx dy \dots(2.47)$$

$$P(x_1, x_2, \dots, x_n, t) = \frac{e^{\sum \alpha_1(t)x_1}}{\phi(\alpha_1(t), \dots, \alpha_n(t))} \dots(2.48)$$

$$\text{where } \phi(a_1(t), \dots, a_n(t)) = \int \dots \int e^{\sum a_i(t)x_i} d\zeta \quad \dots (2.49)$$

$$d\zeta = dx_1 dx_2 \dots dx_n ,$$

with usual interpretation of a 's. In this formulation of probability distribution, the parameters a_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.

2.4 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 the Section-2.3, we may arrive at the Onsager's reciprocal relation, by using very simple mathematical methods. 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

$$\bar{X}(t) = X_0(t) = \frac{\iint x e^{a(t)x+\beta(t)y} dx dy}{\Phi(a(t), \beta(t))} \quad \dots(2.50)$$

$$\bar{Y}(t) = Y_0(t) = \frac{\iint y e^{a(t)x+\beta(t)y} dx dy}{\Phi(a(t), \beta(t))} \quad \dots(2.51)$$

where

$$\Phi \equiv \Phi(a(t), \beta(t)) = \iint e^{a(t)x+\beta(t)y} dx dy \quad \dots(2.52)$$

Now,

$$\frac{\Delta \Phi}{\Phi} = X_0(t) \Delta a + Y_0(t) \Delta \beta \quad \dots(2.53)$$

Again from (2.50)

$$\begin{aligned} \Delta X_0 &= \frac{\delta X_0}{\delta a} \Delta a + \frac{\delta X_0}{\delta \beta} \Delta \beta \\ &= [\bar{X}^2 - (\bar{X})^2] \Delta a + [\iint (xy - X_0 Y_0) P(x,y,t) dx dy] \Delta \beta \end{aligned} \quad \dots(2.54)$$

Then we may write

$$\frac{dX_0}{dt} = [\bar{X}^2 - (\bar{X})^2] \frac{da}{dt} + [\iint (xy - X_0 Y_0) P(x,y,t) dx dy] \frac{d\beta}{dt} \quad \dots(2.55)$$

Similarly it may be proved,

$$\frac{dY_0}{dt} = \left[\iint (xy - X_0 Y_0) P(x,y,t) dx dy \right] \frac{d\alpha}{dt} + \left[\overline{Y^2} - (\bar{Y})^2 \right] \frac{d\beta}{dt} \quad \dots(2.56)$$

Let us denote

$$\frac{dX_0}{dt} = J_1, \quad \frac{dY_0}{dt} = J_2 \quad \dots(2.57a)$$

and

$$\dot{\alpha} \left(= \frac{d\alpha}{dt} \right) = X_1, \quad \dot{\beta} \left(= \frac{d\beta}{dt} \right) = X_2 \quad \dots(2.57b)$$

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

Then (2.55), (2.56) can be written as

$$\left. \begin{aligned} J_1 &= a_{11} X_1 + a_{12} X_2 \\ J_2 &= a_{21} X_1 + a_{22} X_2 \end{aligned} \right\} \quad \dots(2.58)$$

$$\text{where } a_{12} = a_{21} = \iint (xy - X_0 Y_0) P(x,y,t) dx dy, \quad \dots(2.59)$$

which proves Onsager's reciprocal relation. $\dot{\alpha}, \dot{\beta}$, when taken as thermodynamic forces need a bit explanation. It is already interpreted as to how the statistical parameters are identified with

thermodynamic quantities involved in a thermodynamic system in equilibrium, in Section 2.2.4 (Dutta, 1953). According to Section 2.3, the same interpretations are valid, when a non-equilibrium state very near to equilibrium, is considered. 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 α and β are associated with temperature and chemical potential respectively, which are no doubt, intensive thermodynamic variables and hence $\dot{\alpha}, \dot{\beta}$, may without any confusion, be treated as thermodynamic forces causing the fluxes viz. heat flow $(-\frac{dX_0}{dt})$ and mass flow $(-\frac{dY_0}{dt})$.

2.5 THE MOST GENERAL CASE

Assuming that there exist n basic entities in the thermodynamic system under consideration and starting from the probability distribution given in Section 2.3, Onsager's reciprocal relation can be established.

$$\bar{x}_1 = \frac{\int \dots \int x_1 e^{\sum \alpha_i(t) x_i} d\tau}{\phi(\alpha_1(t), \alpha_2(t), \dots, \alpha_n(t))}, \quad i = 1, 2, \dots, n. \quad \dots(2.60)$$

Now,

$$\dot{\phi} = \frac{d\phi}{dt} = \sum_{i=1}^n \frac{\delta\phi}{\delta\alpha_i} \dot{\alpha}_i = \sum_{i=1}^n \left(\int \dots \int x_i e^{\sum \alpha_j(t) x_j} d\tau \right) \dot{\alpha}_i \quad \dots(2.61)$$

where the dot denotes the differentiation w.r.t. t .

Then,

$$\frac{\dot{\phi}}{\phi} = \sum_{i=1}^n \bar{x}_i \dot{a}_i \quad \dots(2.62)$$

$$\begin{aligned} \therefore \frac{d\bar{x}_i}{dt} &= \frac{1}{\phi} \left[\dot{a}_i \int x_1^2 e^{\sum a_1(t)x_1} d\zeta + \sum_{i \neq k} \dot{a}_k \int x_1 x_k e^{\sum a_1(t)x_1} d\zeta \right. \\ &\quad \left. - \sum \dot{a}_j \bar{x}_j \int x_1 e^{\sum a_1(t)x_1} d\zeta \right] \quad \dots(2.63) \end{aligned}$$

$$\begin{aligned} &= \dot{a}_i \left[\int x_1^2 P d\zeta - \left(\int x_1 P d\zeta \right)^2 \right] \\ &\quad + \sum_{\substack{k=1 \\ k \neq i}}^n \dot{a}_k \int (x_1 x_k - \bar{x}_1 \bar{x}_k) P d\zeta, \quad \dots(2.64) \end{aligned}$$

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

$$\begin{aligned} \frac{d\bar{x}_i}{dt} &= \left[\bar{x}_1^2 - (\bar{x}_1)^2 \right] \dot{a}_i + \sum_{\substack{k=1 \\ k \neq i}}^n \dot{a}_k \int (x_1 x_k - \bar{x}_1 \bar{x}_k) P d\zeta, \\ &\quad i = 1, 2, \dots, n \quad \dots(2.65) \end{aligned}$$

This result may be written in the matrix form :

$$J = [a_{ij}] \times \quad \dots(2.66)$$

where

$$J = \begin{bmatrix} \frac{d\bar{x}_1}{dt} \\ \frac{d\bar{x}_2}{dt} \\ \vdots \\ \frac{d\bar{x}_n}{dt} \end{bmatrix} \quad \text{and} \quad X = \begin{bmatrix} \dot{a}_1 \\ \dot{a}_2 \\ \vdots \\ \dot{a}_n \end{bmatrix} \quad \dots(2.67)$$

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

$$a_{11} = \overline{x_1^2} - (\bar{x}_1)^2 \quad \dots(2.68a)$$

$$a_{1j} = \int (x_1 x_j - \bar{x}_1 \bar{x}_j) P d\tau \quad \dots(2.68b)$$

$$a_{j1} = \int (x_j x_1 - \bar{x}_j \bar{x}_1) P d\tau \quad \dots(2.68c)$$

Showing thereby

$$a_{1j} = a_{j1} \quad \dots(2.69)$$

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

2.6 CONCLUDING REMARKS

This essentially stochastic approach to non-equilibrium thermodynamics is proved useful equally well as it yields the most fundamental result of irreversible thermodynamics; the

extra advantage in this development is that, the expressions for the co-efficients, a_{ij} , $i = 1, 2, \dots, n$, $j = 1, 2, \dots, n$, in the Onsager's relation, viz.

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

are obtained; a_{ij} is associated with the correlation co-efficient between the i^{th} and j^{th} entities.