CHAPTER - IV

FLUCTUATION - REVERSIBILITY AND IRREVERSIBILITY

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4.1 INTRODUCTION

From the point of view of statistical mechanics, the statistical averages of the different thermodynamic quantities which are generally known as extensive variables of a thermodynamic system in equilibrium, are generally discussed with interest.

The dispersions or the fluctuations about the average values, however small it may be, are of importance in the analysis of physical phenomena, specially, in those of irreversible type. Fluctuation bears a great significance in some macroscopic experiments too, particularly in the phenomena of phase transition near the critical point.

Schlögl (1971) calculated the probability distribution of the parameter representing fluctuation for a general thermodynamic state, which can be a non-equilibrium state too, with the assumption that to a non-equilibrium state, given by the values of macroscopic variables, there corresponds uniquely a probability distribution and with the use of Renyi's (1966) "information gain".

In our investigation, starting with the probability distribution for the non-equilibrium state, specified by the macroscopic variables and which is derived from a purely stochastic model, we obtain the fluctuation for the extensive thermodynamic variables in that state. We study also as to how the fluctuation in the equilibrium state is modified, when the state of the system deviates from equilibrium.

In the stochastic model, formulated and developed by Dutta (Chapter-II), referred to as Dutta's essentially stochastic model, the basic entities like energy, mass etc., the thermodynamic extensive variables, involved in the system, are considered mutually independent. Dutta (1952-'78), in his theory considered the equilibrium state of an open thermodynamic system and calculated the fluctuations of the basic entities identifiable to thermodynamic extensive variables and also those of the statistical parameters of the probability distributions identifiable to the intensive variables like temperature, chemical potential etc. It is proved by Dutta (1966) and afterwards by Chakrabarti (1970), from different considerations, that when the basic entities are correlated, the standard results for fluctuation of temperature or chemical potential are modified by a multiplicative factor depending on the correlation coefficient.

The theory is extended to the non-equilibrium states, not far from equilibrium (Chapter-II). In this chapter, fluctuations are calculated for the extensive variables when the system undergoes an irreversible process. A generalised result is obtained when all the extensive thermodynamic variables are supposed to be correlated. Fluctuations in the equilibrium state is obtained as a limiting case with interpretations from physical stand-point, in the light of the basic hypothesis of Onsager's theory concerning the cross-effects, existing in the system, when an irreversible process starts.

Fluctuations in the equilibrium states developed by Dutta is discussed in the Section-2.2.6 briefly.

First of all, we shall obtain, for a clear understanding of technique, the fluctuation of a single entity involved in the process of irreversibility by a very simple method. Afterwards we shall pass over to the calculation of the general expression for fluctuations when more than one thermodynamic extensive variables are involved in a system under the process of irreversibility.

4.2 FLUCTUATION OF A SINGLE ENTITY

Let us consider a thermodynamic system in which energy is the only basic entity. The whole system is in contact with a heat bath i.e. the system is open, so far as the exchange of energy is concerned.

In addition to the fundamental assumptions of additivity and conservation (Chapter-II), we assume that the change of energy, very near to equilibrium state occurs very slowly, steadily, so that the energy at the time t, in the system may be given by the equation

$$X_o(t) = X_o(0) + \eta t \quad , \qquad \ldots(4.1)$$

where

$X_o(t)$ = observed value of the energy in the system at the instant t, when t is very small.

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

From (2.50),

$$\bar{X}(t) = X_o(t) = \frac{\int x\, e^{\alpha(t)x}\, dx}{\Phi(\alpha(t))} \quad , \qquad \ldots(4.2)$$

where

$$\Phi(\alpha(t)) = \int e^{\alpha(t)x}\, dx \quad . \qquad \ldots(4.3)$$

Now

$$\frac{\frac{d\Phi(\alpha(t))}{dt}}{\Phi(\alpha(t))} = \frac{\Phi'(\alpha(t))\frac{d\alpha(t)}{dt}}{\Phi(\alpha(t))} = X_o(t)\frac{d\alpha(t)}{dt} \qquad \ldots(4.4)$$

where

$$\Phi'(x) = \frac{d\Phi(x)}{dx}$$

For an infinitesimal change in energy, during an infinitesimal span of time, from (4.1), we get

$$\eta = \frac{dX_o}{dt} \qquad \ldots(4.5)$$

i.e.,

$$\eta = \frac{\Phi(\alpha(t))\left(\frac{d\alpha(t)}{dt}\int x^2 e^{\alpha(t)x}\,dx\right) - \frac{d\Phi(\alpha(t))}{dt}\int x\, e^{\alpha(t)x}\,dx}{(\Phi(\alpha(t)))^2}$$

$$= \left(\overline{X^2} - (\bar{X})^2\right)\frac{d\alpha}{dt} \qquad \ldots(4.6)$$

From (4.5) and (4.6), we get

$$\mathrm{Var}(X) = \overline{X^2} - (\bar{X})^2$$

$$= \frac{\eta}{\frac{d\alpha}{dt}}$$

$$= \frac{\frac{dX_o}{dT}\ \frac{dT}{dt}}{\frac{1}{kT^2}\ \frac{dT}{dt}} = k\,T^2\,C_v \quad , \qquad \ldots(4.7)$$

where C_v is the specific heat at constant volume and $\alpha = -\frac{1}{kT}$ (Sec. 2.2.4 and 2.3).

Equation (4.5) and (4.6) together can be interpreted as the flow of energy is linearly connected with the temperature gradient (Sec. 2.5), which resembles the Fourier's law, between the heat flow and temperature gradient, in the form of proportionality.

The fluctuation of the other basic entities may be obtained by similar method and can be interpreted as the corresponding phenomenological laws in the form of proportionalities like Fick's law, Ohm's law etc.

4.3 FLUCTUATION OF THE ENERGY AND MASS IN AN OPEN SYSTEM

Let two entities X_1, X_2, say, energy and mass respectively, exist in an open thermodynamic system under consideration. Then from the general relation (Chapter-II and III), connecting the thermodynamic fluxes and different thermodynamic gradients, viz.,

$$\frac{d\langle X_i(t)\rangle}{dt} = \left(\langle (X_i(t))^2\rangle - \langle X_i(t)\rangle^2\right)\frac{d\alpha_i}{dt} + \sum_{j,j\neq i}\left\{\sum_n (X_{i,n}X_{j,n} - \langle X_i(t)\rangle\langle X_j(t)\rangle)p_n(t)\right\}\frac{d\alpha_j}{dt} . \qquad ...(4.8)$$

We have,

$$\frac{d\langle X_1\rangle}{dt} = \mathrm{Var}(X_1)\frac{d\alpha_1}{dt} + \mathrm{Cov}(X_1, X_2)\frac{d\alpha_2}{dt} \quad , \quad \ldots(4.9)$$

$$\frac{d\langle X_2\rangle}{dt} = \mathrm{Cov}(X_1, X_2)\frac{d\alpha_1}{dt} + \mathrm{Var}(X_2)\frac{d\alpha_2}{dt} \quad , \quad \ldots(4.10)$$

where $\mathrm{Var}(X_i)$ and $\mathrm{Cov}(X_i, X_j)$ denote the variance of X_i and the covariance of the $i^{\underline{th}}$ and $j^{\underline{th}}$ entities, X_i and X_j respectively.

Since the fluxes are supposed to be independent, the determinant of the coefficient matrix is diffent from zero, (Groot, 1951). Then from (4.9) and (4.10), by using familiar results of statistics,

$$1 - \gamma^2_{X_1,X_2} \neq 0 \quad ,$$

where γ_{X_1,X_2} is the correlation coefficient between the entities X_1 and X_2. For briefity and convenience γ_{X_1,X_2} will be denoted by γ_{12}.

Assuming that the flow of mass is arrested at the particular instant under consideration and eliminating $\frac{d\alpha_2}{dt}$ from (4.9) and (4.10), we get,

$$\frac{d\langle X_1\rangle}{dt} = Var(X_1)\ (1 - \gamma_{12}^2)\ \frac{d\alpha_1}{dt}$$

or
$$Var(X_1) = \frac{C_v\, k\, T^2}{1 - \gamma_{12}^2} \quad . \qquad \ldots(4.11)$$

When $\gamma_{12} = 0$ i.e. X_1, X_2 become uncorrelated, (4.11) becomes

$$Var(X_1) = C_v\, k\, T^2 \quad , \qquad \ldots(4.12)$$

which is the expression for fluctuation of energy, in the equilibrium state for a canonical ensemble.

The results, so far obtained, implies that the basic entities involved in the system can no more be considered mutually independent, when the system is in non-equilibrium state, so that the correlations between them takes an important role in the process and affect considerably the fluctuation of either of the entities.

The obviousness of this result can be justified, if we analyse the basic idea of Onsager's theory of reciprocity and its implication in the mode of approach, we have used in our investigation. In that theory due to Onsager, the quantitative result, viz.,

$$L_{ij} = L_{ji}$$

in the linear relation,

$$J_i = \sum_j L_{ij} X_j ,$$

where J's X's represent fluxes and thermodynamic forces respectively, is based on the hypothesis that the flows or the thermodynamic fluxes are influenced by the cross-effects. In stochastic models, it is evident that the cross-effects will be manifested as the correlation and covariance. As a result, we have got in (4.9) and (4.10) and (2.59), the quantitative results of reciprocity as covariance, viz.,

$$a_{12} = a_{21} = \mathrm{Cov}(X_1, X_2) ,$$

and the thermodynamic fluxes (i.e., the rate of change of the average of the extensive thermodynamic variables) must be affected by the correlation; as such the fluctuation of the corresponding quantity will also involve correlation terms when an irreversible process is going on in the system under consideration.

Chakrabarti (1971) interpreted the presence of the factor $(1 - \gamma_{12}^2)^{-1}$ in the expressions for the fluctuations of the intensive thermodynamic variables like temperature or chemical potential due to the fact that the local inhomogeneity starts as the system deviates from equilibrium state.

From the basic hypotheses of the theory, viz., the flows are independent and the linear relation between the fluxes and the forces is interchangeable, $1 - \gamma_{12}^2 \neq 0$, so that the case when $\gamma_{12}^2 \sim 1$ can not be explained in the light of this theory. The case is also not justifiable from the physical view point as it is obvious from the mathematical expression of (4.11).

This case will be considered seperately in the near future in our next attempt.

Following the similar procedure, the fluctuation of the entity X_2, representing the total number of particles, i.e. the mass in the system, can be calculated.

From (4.9) and (4.10) and assuming that the flow of energy (X_1) is arrested at the particular instant under consideration and then eleminating $\frac{d\alpha_1}{dt}$, we get,

$$\frac{d\langle X_2 \rangle}{dt} = (1 - \gamma_{12}^2) \; \mathrm{Var}(X_2) \; \frac{d\alpha_2}{dt} \quad . \qquad \ldots(4.13)$$

Since $\alpha_2 = \frac{\mu}{k\,T}$, (Sec. 2.2.4 and 2.3) and for a constant T,

$$\mathrm{Var}(X_2) \doteq k\,T \left(\frac{\delta \langle X_2 \rangle}{\delta \mu}\right)_{T,V} \times \frac{1}{1 - \gamma_{12}^2} \quad . \qquad \ldots(4.14)$$

When $\gamma_{12} = 0$ indicating the mutual independence of mass (X_2) and energy (X_1),

$$\mathrm{Var}\,(X_2) = k\,T\,\left(\frac{\delta \langle X_2 \rangle}{\delta \mu}\right)_{T,V} \qquad \ldots(4.15)$$

which is the result for fluctuation in phase population as calculated from grand canonical ensemble.

As in the earlier case, here also it is not possible to interpret the situation, when $\gamma_{12}^2 \sim 1$, till the conditions set up in the theory due to Onsager and in our development too, are satisfied.

4.4 FOR THREE BASIC ENTITIES

Let three basic entities, say, X_1, X_2, X_3, of which X_1 stands for energy, are present in the open system under consideration. Assuming that the flow of the entities represented by X_2 and X_3 are arrested at the particular instant, we get from (4.8)

$$\mathrm{Var}(X_1)\,\frac{d\alpha_1}{dt} + \mathrm{Cov}(X_1, X_2)\,\frac{d\alpha_2}{dt} + \mathrm{Cov}(X_1,X_3)\,\frac{d\alpha_3}{dt} = \frac{d\langle X_1\rangle}{dt} \qquad \ldots(4.16)$$

$$\mathrm{Cov}(X_2,X_1)\,\frac{d\alpha_1}{dt} + \mathrm{Var}(X_2)\,\frac{d\alpha_2}{dt} + \mathrm{Cov}(X_2,X_3)\,\frac{d\alpha_3}{dt} = 0 \qquad \ldots(4.17)$$

$$\mathrm{Cov}(X_3,X_1)\,\frac{d\alpha_1}{dt} + \mathrm{Cov}(X_3,X_2)\,\frac{d\alpha_2}{dt} + \mathrm{Var}(X_3)\,\frac{d\alpha_3}{dt} = 0\ , \qquad \ldots(4.18)$$

or, using the well-known result of statistics, we can write, the above equations as follows :

$$\sigma_1 \frac{d\alpha_1}{dt} + \gamma_{12} \sqrt{\sigma_1 \cdot \sigma_2} \frac{d\alpha_2}{dt} + \gamma_{13} \sqrt{\sigma_1 \sigma_3} \frac{d\alpha_3}{dt} = \frac{d\langle X_1 \rangle}{dt}$$

or,

$$\sqrt{\sigma_1} \frac{d\alpha_1}{dt} + \gamma_{12} \sqrt{\sigma_2} \frac{d\alpha_2}{dt} + \gamma_{13} \sqrt{\sigma_3} \frac{d\alpha_3}{dt} = \frac{1}{\sqrt{\sigma_1}} \frac{d\langle X_1 \rangle}{dt} \qquad \ldots(4.19)$$

Similarly (4.17) and (4.18) become respectively

$$\gamma_{12} \sqrt{\sigma_1} \frac{d\alpha_1}{dt} + \sqrt{\sigma_2} \frac{d\alpha_2}{dt} + \gamma_{23} \sqrt{\sigma_3} \frac{d\alpha_3}{dt} = 0 \qquad \ldots(4.20)$$

and

$$\gamma_{13} \sqrt{\sigma_1} \frac{d\alpha_1}{dt} + \gamma_{23} \sqrt{\sigma_2} \frac{d\alpha_2}{dt} + \sqrt{\sigma_3} \frac{d\alpha_3}{dt} = 0 , \qquad \ldots(4.21)$$

where σ_i denotes the variance of X_i and γ_{ij} denotes the partial correlation coefficient between the entities X_i and X_j .

Now using Cramer's rule, provided

$$\begin{vmatrix} 1 & \gamma_{12} & \gamma_{13} \\ \gamma_{12} & 1 & \gamma_{23} \\ \gamma_{13} & \gamma_{23} & 1 \end{vmatrix} \neq 0$$

we get,

$$\frac{\sqrt{\sigma_1}\ \dfrac{d\alpha_1}{dt}}{\begin{vmatrix} \dfrac{d\langle X_1\rangle}{dt}\cdot\dfrac{1}{\sqrt{\sigma_1}} & \gamma_{12} & \gamma_{13} \\ 0 & 1 & \gamma_{23} \\ 0 & \gamma_{23} & 1 \end{vmatrix}} = \frac{\sqrt{\sigma_2}\ \dfrac{d\alpha_2}{dt}}{\begin{vmatrix} 1 & \dfrac{d\langle X_1\rangle}{dt}\cdot\dfrac{1}{\sqrt{\sigma_1}} & \gamma_{13} \\ \gamma_{12} & 0 & \gamma_{23} \\ \gamma_{13} & 0 & 1 \end{vmatrix}}$$

$$= \frac{\sqrt{\sigma_3}\ \dfrac{d\alpha_3}{dt}}{\begin{vmatrix} 1 & \gamma_{12} & \dfrac{d\langle X_1\rangle}{dt}\cdot\dfrac{1}{\sqrt{\sigma_1}} \\ \gamma_{12} & 1 & 0 \\ \gamma_{13} & \gamma_{23} & 0 \end{vmatrix}} = \frac{1}{\begin{vmatrix} 1 & \gamma_{12} & \gamma_{13} \\ \gamma_{12} & 1 & \gamma_{23} \\ \gamma_{13} & \gamma_{23} & 1 \end{vmatrix}} \qquad \ldots(4.22)$$

Hence,

$$\sqrt{\sigma_1}\ \frac{d\alpha_1}{dt} = \frac{\dfrac{d\langle X_1\rangle}{dt}\cdot\dfrac{1}{\sqrt{\sigma_1}}\,(1-\gamma_{23}^2)}{1-\gamma_{12}^2-\gamma_{23}^2-\gamma_{13}^2+2\gamma_{12}\gamma_{13}\gamma_{23}},$$

so that,

$$\sigma_1 = \frac{1 - \gamma_{23}^2}{1 - \gamma_{12}^2 - \gamma_{23}^2 - \gamma_{13}^2 + 2\gamma_{12}\gamma_{13}\gamma_{23}} \times \frac{\frac{d\langle X_1\rangle}{dT}}{\frac{d\alpha_1}{dT}}$$

i.e.,

$$\mathrm{Var}(X_1) = \frac{1 - \gamma_{23}^2}{1 - \gamma_{12}^2 - \gamma_{23}^2 - \gamma_{13}^2 + 2\gamma_{12}\gamma_{23}\gamma_{13}} \; C_V\, k\, T^2 \quad , \qquad \ldots(4.23)$$

since $\alpha_1 = -\frac{1}{kT}$.

Assuming $\gamma_{23}^2 = 0$, i.e., the entities other than X_1 are mutually independent, we get,

$$\mathrm{Var}\,(X_1) = \frac{C_V\, k\, T^2}{1 - \gamma_{12}^2 - \gamma_{13}^2} \; . \qquad \ldots(4.24)$$

This result is in parity with the result (4.11). Again from (4.23), retaining upto second order terms, we get,

$$\mathrm{Var}\,(X_1) \approx (1 + \gamma_{12}^2 + \gamma_{13}^2) \cdot (C_V\, k\, T^2) \qquad \ldots(4.25)$$

The result (4.25) can also be deduced from (4.24).

Thus, in either case, whether the entities other than X_1 i.e., that entity, whose fluctuation is under consideration, are mutually independent or not, the same expression for the fluctuation is obtained, upto the second order approximation.

4.5 FURTHER GENERALISATION

Let X_i , $i = 1,2, \ldots, n$, are the n basic entities in an open system undergoing an irreversible process, though very near to equilibrium. The postulates set up in the Chapter-II and III are valid in this case also. Furthermore, let us assume,

i) Correlation exists only between the r^{th} entity and the remaining $(n - 1)$ entities; these $(n-1)$ entities other than the r^{th} one are mutually independent among themselves.

ii) The flow of these $(n-1)$ entities, other than r^{th} one are arrested at the particular instant under consideration.

We get from (4.8),

$$\frac{d\langle X_r\rangle}{dt} = \sum_{\substack{k=1 \\ k\neq r}}^{n} \gamma_{rk} (\sigma_r \sigma_k)^{1/2} \frac{d\alpha_k}{dt} + \sigma_r \frac{d\alpha_r}{dt} \qquad \ldots(4.26)$$

$$0 = \gamma_{rk} (\sigma_r \sigma_k)^{1/2} \frac{d\alpha_r}{dt} + \sigma_k \frac{d\alpha_k}{dt} \qquad \ldots(4.27)$$

$$k = 1,2,\ldots,n \; ; \; k \neq r \; .$$

From these n equations, eleminating (n-1) quantities,

$$\frac{d\alpha_k}{dt} \quad , \quad k = 1,2,\ldots, n \;, \quad k \neq r \;,$$

we get,

$$\frac{d\langle X_r\rangle}{dt} = \sigma_r \left(1 - \sum_{\substack{k=1 \\ k\neq r}}^{n} \gamma_{rk}^2 \right) \frac{d\alpha_r}{dt} \;, \qquad \ldots(4.28)$$

i.e.,

$$\sigma_r = \frac{\dfrac{d\langle X_r\rangle}{dt}}{\Delta \dfrac{d\alpha_r}{dt}} \qquad \ldots(4.29a)$$

$$= \frac{\dfrac{d\langle X_r\rangle}{dT}}{\Delta \dfrac{d\alpha_r}{dT}} \;, \qquad \ldots(4.29b)$$

where

$$\Delta = 1 - \sum_{\substack{k=1 \\ k\neq r}}^{n} \gamma_{rk}^2$$

and γ_{rk} is the partial correlation coefficient of the $r^{\underline{th}}$ entity and $k^{\underline{th}}$ entity; σ_r denotes the variance of X_r.

As a particular case if X_r stands for energy, then (4.29b) becomes,

$$\sigma_r = C_v \, k \, T^2 / \Delta \qquad \ldots(4.30)$$

$$\approx C_v \, k \, T^2 \, (1 + \sum_{\substack{k=1 \\ k \neq r}}^{n} \gamma_{rk}^2) \,, \qquad \ldots(4.31)$$

upto second order approximation and assuming $\Sigma \gamma_{rk}^2 < 1$.

4.5.1 <u>When All the Entities are Mutually Correlated</u>.

Let all the basic entities X_i , $i = 1,2,\ldots, n$, are mutually correlated. Under this most general condition, let us obtain the variance of any one of the entities, say, Var (X_r) which is denoted by σ_r .

We get from (4.8), with the assumption (ii) only of Section-4.5 ,

$$\sigma_1 \frac{d\alpha_1}{dt} + \gamma_{12} \sqrt{\sigma_1\sigma_2} \frac{d\alpha_2}{dt} + \ldots + \gamma_{1r}\sqrt{\sigma_1\sigma_r} \frac{d\alpha_r}{dt} + \ldots + \gamma_{1n}\sqrt{\sigma_1\sigma_n} \frac{d\alpha_n}{dt} = 0$$

$$\gamma_{12}\sqrt{\sigma_1\sigma_2} \frac{d\alpha_1}{dt} + \sigma_2 \frac{d\alpha_2}{dt} + \ldots + \gamma_{2r}\sqrt{\sigma_2\sigma_r} \frac{d\alpha_r}{dt} + \ldots + \gamma_{2n}\sqrt{\sigma_2\sigma_n} \frac{d\alpha_n}{dt} = 0$$

$$\ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots$$

$$\gamma_{1r}\sqrt{\sigma_1\sigma_r} \frac{d\alpha_1}{dt} + \gamma_{2r}\sqrt{\sigma_2\sigma_r} \frac{d\alpha_2}{dt} + \ldots + \sigma_r \frac{d\alpha_r}{dt} + \ldots + \gamma_{rn}\sqrt{\sigma_r\sigma_n} \frac{d\alpha_n}{dt} = \frac{d\langle X_r\rangle}{dt}$$

$$\ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots$$

$$\gamma_{1n}\sqrt{\sigma_1\sigma_n} \frac{d\alpha_1}{dt} + \gamma_{2n}\sqrt{\sigma_2\sigma_n} \frac{d\alpha_2}{dt} + \ldots + \gamma_{rn} \sqrt{\sigma_r\sigma_n} \frac{d\alpha_r}{dt} + \ldots + \sigma_n \frac{d\alpha_n}{dt} = 0 \,.$$

Simplifying and denoting $\sqrt{\sigma_r}\ \frac{d\alpha_r}{dt}$ by v_r , $r = 1,2, \ldots, n$,

$$
\begin{aligned}
v_1 + \gamma_{12} v_2 + \cdots + \gamma_{1r} v_r + \cdots + \gamma_{1n} v_n &= 0 \\
\gamma_{12} v_1 + v_2 + \cdots + \gamma_{2r} v_r + \cdots + \gamma_{2n} v_n &= 0 \\
\cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad & \cdots \\
\gamma_{1r} v_1 + \gamma_{2r} v_2 + \cdots + v_r + \cdots \gamma_{rn} v_n &= \frac{1}{\sqrt{\sigma_r}} \cdot \frac{d\langle X_r\rangle}{dt} \\
\cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad & \cdots \quad \cdots \\
\gamma_{1n} v_1 + \gamma_{2n} v_2 + \cdots + \gamma_{rn} v_r + \cdots + v_n &= 0 \quad . \qquad \ldots(4.32)
\end{aligned}
$$

By using Cramer's method, assuming,

$$
D \equiv \begin{vmatrix}
1 & \gamma_{12} & \gamma_{13} & \cdots & \gamma_{1r} & \cdots & \gamma_{1n} \\
\gamma_{12} & 1 & \gamma_{23} & \cdots & \gamma_{2r} & \cdots & \gamma_{2n} \\
\gamma_{13} & \gamma_{23} & 1 & \cdots & \gamma_{3r} & \cdots & \gamma_{3n} \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\gamma_{1r} & \gamma_{2r} & \gamma_{3r} & \cdots & 1 & \cdots & \gamma_{rn} \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\gamma_{1n} & \gamma_{2n} & \gamma_{3n} & \cdots & \gamma_{rn} & \cdots & 1
\end{vmatrix} \neq 0 \qquad \ldots(4.33)
$$

we get

$$\frac{\nu_1}{\begin{vmatrix} 0 & \gamma_{12} & \cdots & \gamma_{1n} \\ 0 & 1 & \cdots & \gamma_{2n} \\ 0 & \gamma_{23} & \cdots & \gamma_{3n} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{d\langle X_r\rangle}{dt}\frac{1}{\sqrt{\sigma_r}} & \gamma_{2r} & \cdots & \gamma_{rn} \\ \cdots & \cdots & \cdots & \cdots \\ 0 & \gamma_{2n} & \cdots & 1 \end{vmatrix}} = \cdots$$

$$\cdots = \frac{\nu_r}{\begin{vmatrix} 1 & \cdots & \gamma_{1(r-1)} & 0 & \cdots & \gamma_{1n} \\ \gamma_{12} & \cdots & \gamma_{2(r-1)} & 0 & \cdots & \gamma_{2n} \\ \gamma_{13} & \cdots & \gamma_{3(r-1)} & 0 & \cdots & \gamma_{3n} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \gamma_{1r} & \cdots & \gamma_{(r-1)r} & \frac{d\langle X_r\rangle}{dt}\frac{1}{\sqrt{\sigma_r}} & \cdots & \gamma_{rn} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \gamma_{1n} & \cdots & \gamma_{(r-1)n} & 0 & \cdots & 1 \end{vmatrix}}$$

$$= \cdots = \frac{1}{D} \qquad \ldots(4.34a)$$

so that

$$v_r = \frac{1}{D} \begin{vmatrix} 1 & \cdots & \gamma_{1(r-1)} & 0 & \cdots & \gamma_{1n} \\ \gamma_{12} & \cdots & \gamma_{2(r-1)} & 0 & \cdots & \gamma_{2n} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \gamma_{1r} & \cdots & \gamma_{(r-1)r} & \frac{d\langle X_r\rangle}{dt}\frac{1}{\sqrt{\sigma_r}} & \cdots & \gamma_{rn} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \gamma_{1n} & \cdots & \gamma_{(r-1)n} & 0 & \cdots & 1 \end{vmatrix}$$

...(4.34b)

Putting the value of v_r and simplifying, we get,

$$\sigma_r = \left(\frac{d\langle X_r\rangle}{dt} \Big/ \frac{d\alpha_r}{dt} \right) . \frac{A_{rr}}{D}$$

$$= \frac{d\langle X_r\rangle}{d\alpha_r} . \frac{A_{rr}}{D} , \qquad ...(4.35)$$

where A_{ij} denotes the cofactor of $ij^{\underline{th}}$ element in the determinant D, in (4.33), i.e.,

$$A_{rr} = (-1)^{2r} \begin{vmatrix} 1 & \gamma_{12} & \cdots \gamma_{1(r-1)} & \gamma_{1(r+1)} & \cdots \gamma_{1n} \\ \gamma_{12} & 1 & \cdots \gamma_{2(r-1)} & \gamma_{2(r+1)} & \cdots \gamma_{2n} \\ \cdots & \cdots & \cdots \quad \cdots & \cdots & \cdots \quad \cdots \\ \gamma_{1(r-1)} & \gamma_{2(r-1)} & \cdots \quad 1 & \gamma_{(r-1)(r+1)} & \cdots \gamma_{(r-1)n} \\ \gamma_{1(r+1)} & \gamma_{2(r+1)} & \cdots \gamma_{(r-1)(r+1)} & 1 & \cdots \gamma_{(r+1)n} \\ \cdots & \cdots & \cdots \quad \cdots & \cdots & \cdots \quad \cdots \\ \gamma_{1n} & \gamma_{2n} & \cdots \gamma_{(r-1)n} & \gamma_{(r+1)n} & \cdots \quad 1 \end{vmatrix}$$

The result (4.35) gives the most general expression for the fluctuation of $r^{\underline{th}}$ entity .

If in particular, X_r represents the energy of the system, then

$$\sigma_r = \frac{A_{rr}}{D} \left(\frac{d \langle X_r \rangle}{dT} \Big/ \frac{d\alpha_r}{dT} \right) \qquad \ldots(4.36a)$$

$$= \frac{A_{rr}}{D} \cdot C_v \, k \, T^2 \quad , \qquad \ldots(4.26b)$$

where D denotes the symmetric determinant of $n^{\underline{th}}$ order formed with the n partial correlation coefficients, given by (4.33).

The mutual independence of all the basic entities, gives rise to the result,

$$\sigma_r = C_v \ k T^2 \quad .$$

In this connection the following may be noted.

4.5.2 Fluctuation of an Entity, When the System is in Equilibrium

When the system is in equilibrium, taking the probability distribution 2.45 (or 3.6) we have,

$$\langle X_i \rangle = \frac{\int .. \int X_i e^{\sum_r \alpha_r X_r} d\zeta}{\Phi(\alpha_1, \ldots, \alpha_n)} \quad , \text{ where } \Phi(\alpha_1, \ldots, \alpha_n) = \int \ldots \int e^{\sum_r \alpha_r X_r} d\zeta$$

$$d\zeta = dX_1 dX_2 \ldots dX_n \, .$$

Deriving both sides w.r.t. α_i ,

$$\frac{\delta \langle X_i \rangle}{\delta \alpha_i} = \frac{\frac{\delta}{\delta \alpha_i}\left\{ \int .. \int X_i \ e^{\sum_r \alpha_r X_r} \ d\zeta \right\} \Phi - \frac{\delta \Phi}{\delta \alpha_i} \left\{ \int .. \int X_i \ e^{\sum_r \alpha_r X_r} \ d\zeta \right\}}{\left\{ \Phi \ (\alpha_1, \ldots, \alpha_n) \right\}^2}$$

$$= \frac{\int .. \int X_i^2 \ e^{\sum_r \alpha_r X_r} \ d\zeta}{\Phi(\alpha_1, \ldots, \alpha_n)} - \left\{ \frac{\int .. \int X_i \ e^{\sum_r \alpha_r X_r} \ d\zeta}{\Phi(\alpha_1, \ldots, \alpha_n)} \right\}^2$$

$$= \langle X_i^2 \rangle - \langle X_i \rangle^2 \qquad \ldots (4.37)$$

which gives the fluctuation of i^{th} entity in the presence of n entities, X_r , $r = 1, 2, \ldots, n$ in the system.

When X_1 stands for energy, $\alpha_1 = - 1/kT$, and we get

$$\langle X_1^2 \rangle - \langle X_1 \rangle^2 = \frac{\delta \langle X_1 \rangle}{\delta \alpha_1}$$

$$= \frac{d \langle X_1 \rangle}{dT} kT^2$$

$$= C_v \, kT^2 \quad . \qquad \ldots(4.37a)$$

The comparison between the equations (4.37) and (4.35) and for a particular case, viz. for energy, equations (4.37a) and (4.36a) establish directly, how fluctuation of an entity is affected when the system passes over from reversibility to irreversibility.

4.5.3 Observations

(i) $D \neq 0$, where D is given by (4.33). From (4.35), this is obvious from physical consideration too. This condition is evident from (4.8) in the light of the theory concerned in our investigation.

(ii) From (4.29), $\sum_{\substack{k=1 \\ k \neq r}}^{n} Y_{rk}^2 < 1$, from the point of view of physical consistency.

(iii) The assumption (ii) in section 4.5, which is used throughout the development of this chapter, is consistent, as the flows of the thermodynamic entities are supposed to be independent.

(iv) When the system is in non-equilibrium state, then $\Upsilon_{rk} \neq 0$. The results obtained in this chapter coincide with those for equilibrium state, when $\Upsilon_{rk} = 0$.

(v) The emergence of the correlation terms in the expression for the fluctuation is due to irreversibility, not due to mere presence of a number of entities in the system.

(vi) Fluctuation increases when an irreversible process starts in the system.

4.6 CONCLUSIONS

Thus it is clear from the discussion of this chapter that the fluctuation of any entity in an open system is, in general, affected considerably when the system passes over from reversibility to irreversibility; and the correlation among the entities takes an important role due to the cross-effects when the irreversible process is going on.