XII. IRREVERSIBLE THERMODYNAMICS

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It was reported in the Quarterly Progress Report of January 15, 1956, that the fluctuation behavior of a thermodynamic system can be determined if the system is described by a linear phenomenological kinetic equation the coefficients of which form a symmetric matrix.

We applied the general theory to a spatially extended closed system by considering that the system is composed of a linear chain of volume elements; that is, we consider variation only in one spatial direction. We take these volume elements, which are referred to as "cells," to be small compared with the system but to contain a large number of particles.

Let there be N cells. Let the thermodynamic variable under consideration be denoted by a. And let

$$a_j(t) = \text{value of } a \text{ in cell } j \text{ at time } t \qquad (j = 1, 2, \ldots, N)$$

We assume that a is a conserved quantity (i.e., energy, number of particles charge, and so forth). This implies the use of the continuity equations:

$$\dot{a}_1 = -J_1$$

$$\dot{a}_j = J_{j-1} - J_j \qquad (j = 2, 3, \ldots, N-1) \qquad (1)$$

$$\dot{a}_n = J_{N-1}$$

where J_j is the current from cell j to cell $j + 1$.

Equations 1 yield

$$\sum_{j=1}^{N} a_j = \text{constant} \qquad (2)$$

By defining a as the deviation from equilibrium, we can set the constant in Eq. 2 to zero.

We can say that the entropy of the entire system is given by

$$\mathcal{S} = S_1(a_1) + S_2(a_2) + \ldots + S_N(a_N) \qquad (3)$$

and we define the force as

$$F_j = \frac{\partial \mathcal{S}}{\partial a_j} = \frac{\partial S_j}{\partial a_j} \qquad (4)$$

At equilibrium all the F's are equal.

Expanding $\mathcal{S}$ about equilibrium, we obtain

$$\mathcal{S} = \mathcal{S}_o - \frac{1}{2} \Sigma \ s_j \ a_j^2 \tag{5}$$

where

$$s_j = - \frac{\partial^2 S_j}{\partial a_j^2} \tag{6}$$

Therefore, from Eq. 4,

$$F_j = -s_j \ a_j \tag{7}$$

We hypothesize the phenomenological kinetic equations for the system as

$$R_j J_j = F_j - F_{j+1} \tag{8}$$

where R_j is a real positive "resistance" encountered by the current J_j.

If we invert Eqs. 1 and use Eq. 7, we get

$$R_j(\dot{a}_1 + \dot{a}_2 + \ldots + \dot{a}_j) = s_j \ a_j - s_{j+1} \ a_{j+1} \qquad (j = 1, \ldots, N-1) \tag{9}$$

If we use relation 2 and rearrange Eq. 9, we get, in matrix form,

$$\mathcal{R}\dot{a} = \mathcal{S}a \tag{10}$$

where

$$\mathcal{R} = \begin{bmatrix} (R_1 + \ldots + R_{N-1}) & (R_2 + \ldots + R_{N-1}) & \cdots & R_{N-1} \\ (R_2 + \ldots + R_{N-1}) & (R_2 + \ldots + R_{N-1}) & \cdots & R_{N-1} \\ \cdots & & & \\ R_{N-1} & R_{N-1} & \cdots & R_{N-1} \end{bmatrix} ; \quad \mathcal{S} = \begin{bmatrix} S_1 + S_N & S_N & \cdots & S_N \\ S_N & S_2 + S_N & \cdots & S_N \\ \cdots & & & \\ S_N & S_N & \cdots & S_{N-1} + S_N \end{bmatrix} \tag{11}$$

We see from Eqs. 10 and 11 that we can symmetrize the equations even for unequal cells. Thus the formalism outlined in earlier progress reports can be used to obtain space-time fluctuations.

It is interesting to note that the a's are coupled, even though we assume that there is no direct interaction between cells in computing the entropy (or equivalently, the energy) in Eq. 3. The coupling arises from the use of currents and the continuity equation.

The solution to Eq. 10 can be carried out formally. We can obtain the description of the fluctuations in the frequency or time domain, the generating function of the distribution, the correlation coefficients, and so forth. However, in order to achieve a more workable solution, we reduced the equations to the equal-cell case. Even then, the results are too complicated to be discussed in this report.

The kinetic equation 10 can easily be shown to approximate the diffusion equation; and a relation between the diffusion constant and the parameters of Eq. 10 can be obtained.

We can also show that the distribution obtained from this method is truly the solution to the Fokker-Planck equation (as it must be for consistency).

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