# XV. IRREVERSIBLE THERMODYNAMICS

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## A. THEORY OF THERMAL NOISE

This project is a continuation of work begun by L. Tisza and I. Manning in connection with Manning's Ph.D. thesis submitted to the Department of Physics at the Massachusetts Institute of Technology in June 1955 (1). A paper is being prepared for publication. The present report summarizes the results that will be presented in that paper and outlines briefly some problems that are now under consideration.

The phenomenological equations of irreversible thermodynamics connecting the "fluxes" and "forces" represent only statistical averages. The time-dependent fluctuations around the macroscopic force-flux distribution are called thermal noise. The standard method of "saving" the validity of the phenomenological equations is to insert a random function representing a noise generator. The spectral density of the latter has to be ascertained from other considerations.

In this project the problem is considered from another point of view. We shall formulate a variational principle having the following properties:

1. The solutions of the macroscopic kinetic equations render the variational functional a minimum.

2. The manifold of trial functions corresponds to the actual fluctuation paths of the system. The probability density in this manifold is determined by the variational functional.

Let us consider a thermodynamic system in which an irreversible process is described in terms of phenomenological kinetic equations:

$$\sum_{k=1}^{n} R_{ik} J_k = X_i \qquad i = 1, 2, \ldots, n \tag{1}$$

where the $J_k$, $X_k$ are the fluxes and conjugate forces, and $R_{ik}$ is the resistance matrix. The conditions for the Onsager symmetry relations $R_{ik} = R_{ki}$ are assumed to be satisfied. The indices refer to n terminal pairs at which the system interacts with reservoir pairs (generators). The variables are so defined that the rate of entropy production is

$$S = \sum J_i X_i \tag{2}$$

For instance, if J is the energy current, $X = \Delta\left(\frac{1}{T}\right)$, when T is the absolute temperature; but if J is the electric current, $\Delta V = -TX$ becomes the potential difference, and $\mathscr{R} = TR$ the conventional resistance matrix.

Following Onsager and Machlup (2) we define the functional

$$\Gamma = \frac{1}{4}(RJ - X)_{tr} R^{-1} (RJ - X) \tag{3}$$

In this matrix equation tr means transpose, X is a column vector, and $X_{tr}$ is a row vector.

It is obvious that $\Gamma \geqslant 0$, and $\Gamma_{min}$ is attained for the X, J values satisfying Eq. 1. The functional $\Gamma$ also determines the distribution of the fluctuation paths. In fact, the following distribution function can be established for the relative probability of fluctuation paths:

$$e^{-\frac{1}{k}\int_0^\theta \Gamma \, dt} \tag{4}$$

where k is Boltzmann's constant, and $\theta$ is a long interval of time.

Let us assume that the currents J are fixed (by constant-current generators) and the fluctuations of the $X_i$ are

$$\Delta X_i = \sum_{n=1}^{N} \left(\alpha_n \cos \frac{2\pi\, nt}{\theta} + \beta_n \sin \frac{2\pi\, nt}{\theta}\right) \tag{5}$$

If we insert Eq. 5 in Eq. 4 and use Eq. 3, a gaussian distribution for the Fourier coefficients $\alpha_n$, $\beta_n$ is obtained, and the Nyquist expression for the correlation in the frequency band $\nu$, $\nu + \Delta\nu$ is easily derived:

$$\overline{\Delta X_i \Delta X_j} = 4kR_{ij} \tag{6}$$

A number of other fluctuation formulas can be derived, including those for reactive systems. In the latter case the variational functional is defined as

$$\Gamma_t = \frac{1}{4}(R\dot{Q} - \xi)_{tr} R^{-1}(R\dot{Q} - \xi) \tag{7}$$

where $\dot{Q} = J$ and

$$\xi = X - (M\ddot{Q} + SQ) \tag{8}$$

Here M and S are the "inertial" (inductive) and "potential" (capacitive) matrices. Physically $\xi$ would correspond to the potential drop across the resistor in the meshes of the network.

The subscript in $\Gamma_t$ indicates that the functional is in the time domain. It is convenient to consider also the functional in the frequency domain $\Gamma_\omega$, when, with Z the impedance matrix, we obtain

$$\Gamma_\omega = \frac{1}{4} (ZJ - X)^*_{tr} R^{-1} (ZJ - X) \tag{9}$$

The asterisk stands for conjugate complex. Then, we have

$$\int_0^\theta \Gamma_t \, dt = \int_{-\infty}^{\infty} \Gamma_\omega \, d\omega \tag{10}$$

and the minimum principle for $\int_0^\theta \Gamma_t \, dt$ implies that $\Gamma_\omega$ is a minimum.

The functional $\Gamma$ is fundamental to the entire theory, hence its properties are obviously of interest. We have found, in particular, two interesting results:

1. $\Gamma_\omega$ is a minimum for all sorts of boundary conditions. We can fix any linear combinations of J and X and show that the minimization of $\Gamma_\omega$ under these conditions leads to the correct kinetic equations.

2. $\Gamma_\omega$ is an additive quantity. If n terminal components are connected in cascade or in parallel, the $\Gamma_\omega$ of the entire system is the sum of the $\Gamma_\omega$ of the components.

The last result is particularly significant, since propagation and space-time correlation problems may be studied with such composite systems. This matter is now under investigation.

## References

1. See also, Phys. Rev. 98, 1165 (1955).
2. L. Onsager and S. Machlup, Phys. Rev. 91, 1505; 1512 (1953).