XIII. IRREVERSIBLE THERMODYNAMICS

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A. ON THE DISTRIBUTION OF FLUCTUATION PATHS

The study of the fluctuation theory, summarized in the Quarterly Progress Report of January 15, 1956, was extended in two directions. The application of the theory to spatially extended systems is surveyed in Section B. In addition, the foundation of the theory and its relation to earlier theories are reconsidered. This work, which was carried out in collaboration with Dr. I. Manning (now at Syracuse University), is practically complete. A brief summary of our conclusions follows.

Thermodynamic fluctuation theory falls into two divisions. Static theory is concerned with the distribution of fluctuating quantities at a single instant. Kinetic theory considers the temporal sequence of fluctuating values, i. e., the distribution of fluctuation paths. Static theory centers around Boltzmann's principle which establishes a relation between the entropy and the probability of states of "restrained equilibrium."

Recently, Onsager and Machlup (1) proved a theorem that is the kinetic analog of Boltzmann's principle. They related the joint and conditional probability density function of a fluctuating quantity at successive instances to a functional constructed of phenomenological quantities. This functional Γ was defined in Eq. 3 in the Quarterly Progress Report, January 15, 1956, page 125.

The present project is concerned with the further development of the Onsager-Machlup theorem. It appears that the analogy with Boltzmann's principle can be carried to considerable length, although new problems arise in connection with the time dependence of the kinetic theory.

The most obvious application is the calculation of averages over fluctuation paths. The conclusions given in our previous report indicate that these calculations lead to results that are usually obtained by more complicated methods. It is essential to describe the fluctuation paths in terms of their spectral representation by using the method of Rice. Onsager and Machlup established their probability density functions in the temporal description. The first problem was concerned with showing that the same functional can be used as the basis for both types of representation. Several attempts were made to prove this conclusion, which is by no means obvious. The proof which we believe is most satisfactory operates with the characteristic function of distributions.

Finally, we found an alternative derivation of Onsager's and Machlup's temporal probability density function. The proof originates in the analysis of the following paradox: On the one hand, fluctuation paths are assumed to be symmetric with respect to the operation that reverses the sense of time, $t \rightarrow -t$. On the other hand, it is a usual assumption in irreversible thermodynamics that, on the average, the regression of fluctuations follows the macroscopic kinetic equation. However, the solutions of the kinetic equation are not symmetric with respect to time. Although the Onsager-Machlup theory implies that it is not inconsistent to mix the time-symmetric and asymmetric aspects of the theory, it is still of interest to make this consistency more explicit.

Our derivation of the probability density function is based essentially on the analysis of time symmetry. One can show that in a certain sense fluctuation paths can be represented as a combination of falling and rising exponentials corresponding to the regular and the time-reversed solutions of the kinetic equation. Inserting these functions into the functional $\Gamma(\alpha\dot{\alpha})$, we notice that the latter acts like a "filter": the expression

$$\int_{t_1}^{t_2} \Gamma \, dt$$

is equal to the entropy decrease produced by the time reversed contributions, while the entropy increase caused by the regular paths remains unregistered.

It is possible to represent the fluctuation paths in a time-symmetric fashion, and incorporate in the theory a bias in favor of the forward paths by means of a probability density function that is some functional of $\int \Gamma \, dt$. If this qualitative assumption is granted, the quantitative form of the probability density function can be derived from generally accepted principles. The result is precisely the Onsager-Machlup probability density function which was derived originally by another method.

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References

1. L. Onsager and S. Machlup, Phys. Rev. 91, 1505; 1512 (1953).

B. SPACE-TIME CORRELATIONS IN IRREVERSIBLE THERMODYNAMICS

Irreversible thermodynamics is usually discussed in terms of discrete or continuous systems. In the former case, there is a single variable α that describes the deviation of an extensive variable from its equilibrium value. In the continuous system, α is a continuous function of the spatial coordinates. The stochastic methods for the calculation of fluctuations were developed only for discrete systems. Extension of this theory to the continuous case seems to be blocked by serious difficulties.

Nevertheless, there are meaningful problems that would call for the inclusion of spatial extension in the theory. Instead of considering correlation matrices only in the time-variable sense, we may want to discuss space-time correlations. There are propagation problems that are described phenomenologically by the diffusion differential equation and by the wave equation with a damping term.

It is possible to attack problems of this sort by means of the "cellular method" (1). Instead of dividing the thermodynamic system into two subsystems, we consider a division into a large number of identical cells. The fluctuation of a variable is described by a "vector" $\{\alpha_i\}$, where the index i runs over all the cells.

The method of computing correlation coefficients which was discussed in the January report can be applied to this case. Assuming that periodic boundary conditions exist, the system takes on a lattice type of translational symmetry and the matrices occurring in the theory can be simultaneously diagonalized; thus a solution in closed form is obtained. In such a way, we arrive at a formal solution of the space-time problems.

The derivation of partial differential equations, such as the diffusion equation, requires that the size of the cell be small compared with the macroscopic dimensions of the system. It is interesting that letting the size of the cell tend to zero leads to conceptual difficulties. The fractional fluctuation increases as the cellular division becomes finer, hence we are faced with the limitation of the semiphenomenological theory.

The case of small cell sizes appears to be the most interesting problem for further study.

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References

1. M. J. Klein and L. Tisza, Phys. Rev. 76, 1861 (1949).