

it stands whether or not the state is completely specified at each instant. It therefore describes the statistics of sets of variables which are not necessarily Markoffian, but which are sub-sets of Markoffian sets for which the coefficients of the entropy and dissipation functions are known.

### Principle of Least Dissipation

The principle of least dissipation (RRIP I), a generalization of a similar principle in hydrodynamics due to Rayleigh,<sup>18</sup> can be read by inspection from (4-18). Given a state  $\alpha$ , we ask for the most probable values of the  $\alpha$ 's (and thus for the most probable path of the  $\alpha$ 's in time). Taking  $t_2$  close to  $t_1$  ( $t_2 - t_1 = \Delta t = \text{small}$ ) we seek the state  $\alpha^{(2)}$  which will maximize the exponent. The integral becomes a simple product:

$$-\frac{1}{4k} \left[ 2\Phi(d\alpha/dt, d\alpha/dt) + 2\Psi(\mathbf{X}, \mathbf{X}) - 2\frac{d}{dt}S(\alpha) \right] \Delta t = \text{max.} \quad (4-24)$$

If we remember that the variation is with respect to

<sup>18</sup> Lord Rayleigh (J. W. Strutt), *Phil. Mag.* **26**, 776 (1913).

the  $\alpha$ 's only, we have

$$\dot{S} - \Phi(d\alpha/dt, d\alpha/dt) = \text{max.} \quad (4-25)$$

This variational principle is formally equivalent to the phenomenological laws [(2-2), including the reciprocal relations (2-4)].

### Spectral Description

It may be useful to recall the connection between this work and that of Callen and his co-workers in the same field.<sup>19</sup> The systems treated are of the same type, and the same physical assumptions are made for them. But while this paper uses a *temporal* description of the course of fluctuations, these other papers use a *spectral* description. The two descriptions correspond to two types of experiment: the temporal to taking successive readings at close intervals, obtaining, for instance, a trace on a moving tape; the spectral to recording by means of a frequency analyzer. Where in the temporal description we postulate linear relations between forces and fluxes, defined by the dissipation matrix  $\mathbf{R}$ , the spectral description has linear relations between their Fourier transforms, defined by an admittance matrix.

<sup>19</sup> Footnote 13. See also H. Takasi, *J. Phys. Soc. Japan* **7**, 439 (1952).

## Fluctuations and Irreversible Process. II. Systems with Kinetic Energy\*

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(Received May 13, 1953).

The results of the previous paper are extended to second-order systems, i.e., systems with inertia. Using a generalized definition of the thermodynamic forces, reciprocal relations for the dissipative coefficients in the equations describing irreversible processes are derived. A dissipation function can again be defined, and it can again be used to express the probability functional for fluctuations.

### 1. $\beta$ -TYPE VARIABLES

IN the previous paper of the same principal title<sup>1</sup> the thermodynamic variables treated were limited to those satisfying the hypothesis of microscopic reversibility. The restriction was stated: on a kinetic model, the thermodynamic variables must be algebraic sums of (a large number of) molecular variables, and must be *even* functions of those molecular variables which are odd functions of time (like molecular velocities). Thus

\* Much of the work reported in this paper appears in more detail in a dissertation by one of us (S.M.), presented to the Faculty of the Graduate School of Yale University (1952) in partial fulfillment of the requirements for the Ph.D. degree.

<sup>1</sup> L. Onsager and S. Machlup, preceding paper [*Phys. Rev.* **91**, 1505 (1953)].

a reversal of the sense of time would not change the values of these  $\alpha$  variables.

It was assumed that all thermodynamic functions (specifically, the entropy  $S$ ) were given as functions of the  $\alpha$  variables, and that the irreversible processes were "caused" by thermodynamic forces  $X_i = \partial S / \partial \alpha_i$ . If, however, the kinetic energy of the various flows (e.g., magnetic energy of electric currents) contributes appreciably to the entropy, other variables must be taken into consideration: "velocity" variables, i.e., variables which would change their sign if the sense of time were reversed. Casimir<sup>2</sup> calls them  $\beta$  variables. He points

<sup>2</sup> H. B. G. Casimir, *Revs. Modern Phys.* **17**, 343 (1945).

out that for irreversible processes involving both  $\alpha$ 's and  $\beta$ 's, the principle of microscopic reversibility implies that the reciprocal relations have negative signs for the coefficients giving cross phenomena between  $\alpha$  and  $\beta$  variables.

The  $\beta$  variables, which arise from the *inertia* of the system, can be expressed as time derivatives of  $\alpha$ -type variables. The phenomenological laws for irreversible processes, which would be a set of first-order differential equations in the  $\alpha$  and  $\beta$  variables, can thus be written as a set of second-order equations in the  $\alpha$ 's. (Example: a simple electric circuit containing inductance, capacitance and resistance can be described by two first-order equations in charge and current, or by one second-order equation in charge.)

**Phenomenological Laws**

Thus, the entropy is now a function of the  $\alpha$ 's and the  $\dot{\alpha}$ 's. Both are now the variables of state. We would like to have the phenomenological laws in the form

$$\sum_j R_{ij} \dot{\alpha}_j = \xi_i, \quad i = 1 \cdots n \tag{1-1}$$

again. We can achieve this by defining the thermodynamic forces as

$$\xi_i = \frac{\partial S}{\partial \alpha_i} + \frac{dt}{dt} \frac{\partial S}{\partial \dot{\alpha}_i} \tag{1-2}$$

The second member of this sum is analogous to a d'Alembert force in mechanics; it is the second-order term in (1-1). The  $\alpha$ 's are still taken to be zero at equilibrium; the  $\dot{\alpha}$ 's vanish there by their nature.  $S_0 - S$  is again a homogeneous quadratic function of all the variables of state, but there are no cross terms between  $\alpha$ 's and  $\dot{\alpha}$ 's. For the entropy must not change with a reversal of the sense of time: In the microscopic description, the Hamiltonian is an even function of molecular momenta. One may, therefore, think of the entropy as consisting of a "potential" and a "kinetic" part:

$$S = S_0 - \frac{1}{2} \sum_{ij} s_{ij} \alpha_i \alpha_j - \frac{1}{2} \sum_{ij} m_{ij} \dot{\alpha}_i \dot{\alpha}_j \tag{1-3}$$

(The letter  $m$  has been chosen because of the analogy to *mass*.) The phenomenological laws (1-1) become

$$\sum_j (m_{ij} \ddot{\alpha}_j + R_{ij} \dot{\alpha}_j + s_{ij} \alpha_j) = 0, \quad i = 1 \cdots n, \tag{1-4}$$

or, in matrix notation,

$$m\ddot{\alpha} + R\dot{\alpha} + s\alpha = 0. \tag{1-4'}$$

[Henceforth, when appearing without subscript, Greek letters  $\alpha, \epsilon, \xi$  are vectors, Roman  $s, m, R, A, B, C$  are matrices.]

**2. LINEAR SECOND-ORDER STOCHASTIC PROCESS**

We shall again postulate that the average regressions from a given nonequilibrium state obey the same laws as the corresponding irreversible processes, i.e., the

phenomenological laws (1-4). This applies here to the average regressions of the  $\alpha$ 's and the  $\dot{\alpha}$ 's. If we also assume that the fluctuations are Gaussian stochastic processes, then we arrive, as in I, at the conclusion that they are Markoffian—in the  $\alpha$ 's and  $\dot{\alpha}$ 's. Alternatively stated, they are second order stochastic processes in the  $\alpha$ 's alone. They obey, then, the stochastic differential equations,

$$m\ddot{\alpha} + R\dot{\alpha} + s\alpha = \epsilon, \tag{2-1}$$

with the  $\epsilon$ 's purely random impulses. We need only consider the  $n$  equations (1-4) split up into  $2n$  first-order equations in the  $\alpha$ 's and  $\dot{\alpha}$ 's; then the proof by Doob cited in I, Sec. 3, again becomes applicable.

To prove reciprocal relations for the  $R$  matrix, we shall study the second moments and apply microscopic reversibility to them. There are four covariance matrices,

$$\begin{aligned} A(\tau) &= \langle \alpha(t) \alpha_{tr}(t+\tau) \rangle, \\ B(\tau) &= \langle \dot{\alpha}(t) \alpha_{tr}(t+\tau) \rangle, \\ B'(\tau) &= \langle \alpha(t) \dot{\alpha}_{tr}(t+\tau) \rangle, \\ C(\tau) &= \langle \dot{\alpha}(t) \dot{\alpha}_{tr}(t+\tau) \rangle. \end{aligned} \tag{2-2}$$

[Matrix notation:  $tr$  means *transpose*. If  $\alpha$  is a column vector,  $\alpha_{tr}$  is a row vector—e.g.,  $A_{ij}(\tau) = \langle \alpha_i(t) \alpha_j(t+\tau) \rangle$ .] These are related as follows:

$$B(\tau) = -B'(\tau), \quad B(\tau) = -\dot{A}(\tau), \quad C(\tau) = \dot{B}(\tau). \tag{2-3}$$

If we multiply 2-1 by  $\alpha_{tr}(t-\tau)$  on the right, and take averages, we obtain the matrix equation

$$m(d^2A/dt^2)_{tr} + R\dot{A}_{tr} = sA_{tr} = 0, \tag{2-4}$$

the right-hand side vanishing because, by hypothesis, the  $\epsilon$ 's are uncorrelated with the  $\alpha$ 's and  $\dot{\alpha}$ 's. Similarly, if we multiply by  $\dot{\alpha}_{tr}(t-\tau)$ ,

$$m(d^2B/dt^2)_{tr} + R\dot{B}_{tr} + sB_{tr} = 0. \tag{2-5}$$

If we use (2-3), these two sets of  $n^2$  simultaneous second-order equations become two sets of  $2n^2$  simultaneous first-order equations:

$$\dot{A}_{tr} + B_{tr} = 0, \tag{2-6}$$

$$sA_{tr} - m\dot{B}_{tr} - RB_{tr} = 0, \tag{2-7}$$

$$\dot{B}_{tr} + C_{tr} = 0, \tag{2-8}$$

$$sB_{tr} - m\dot{C}_{tr} - RC_{tr} = 0, \tag{2-9}$$

The one-gate distribution function of the  $\alpha$ 's and  $\dot{\alpha}$ 's we know from (1-3) by Boltzmann's principle. The second moments of a Gaussian distribution are given by the reciprocal of the matrix defining the quadratic form in the p.d.f. (probability density function):

$$A(0) = ks^{-1}, \tag{2-10}$$

$$B(0) = B'(0) = 0, \tag{2-11}$$

(no cross-terms in 1-3)

$$C(0) = km^{-1}. \tag{2-12}$$

These equations give the initial conditions for (2-6) to (2-9). We must be careful about evaluating the covariances at  $\tau=0$ , since their derivatives need not be continuous there. Specifying approach from positive  $\tau$ , and substituting (2-11) and (2-12), we obtain from (2-9) a statistical interpretation of the coefficients  $R_{ij}$ :

$$\dot{C}_{ir}(0+) = -km^{-1}Rm^{-1}. \tag{2-13}$$

Had we approached  $\tau=0$  from negative values, we would have obtained the opposite sign in this equation. The derivatives of the  $A_{ij}(\tau)$ , which are discontinuous at  $\tau=0$  in the case without inertia, now vanish there when the  $m$  matrix is positive definite: inertia "smoothes" the correlation between the  $\alpha$ 's.

**Reciprocal Relations**

The principle of microscopic reversibility (see RRIP II) requires that the matrix  $A(\tau)$  be symmetric; hence, by (2-3),  $C(\tau)$  is symmetric.  $m$ , as the matrix of a quadratic form, is by nature symmetric. Thus, from (2-13) follow the reciprocal relations for the  $R_{ij}$ :

$$R = R_{tr}. \tag{2-14}$$

With  $R$  symmetric, a dissipation function,

$$\Phi(\dot{\alpha}, \dot{\alpha}) = \frac{1}{2} \dot{\alpha}_{tr} R \dot{\alpha}, \tag{2-15}$$

can again be defined, having all the properties of the dissipation function of I. For irreversible processes obeying (1-1), the rate of production of entropy is

$$\begin{aligned} \dot{S} &= -\sum_{ij} m_{ij} \dot{\alpha}_i \ddot{\alpha}_j - \sum_{ij} s_{ij} \alpha_i \dot{\alpha}_j \\ &= -\sum_{ij} (m_{ij} \ddot{\alpha}_j + s_{ij} \alpha_j) \dot{\alpha}_i = \sum_i \xi_i \dot{\alpha}_i \\ &= 2\Phi(\dot{\alpha}, \dot{\alpha}) = 2\Psi(\xi, \xi), \end{aligned} \tag{2-16}$$

where the function

$$\Psi(\xi, \xi) = \frac{1}{2} \xi_{tr} R^{-1} \xi \tag{2-17}$$

is also the natural extension of its counterpart in I.

**3. INTEGRAL FORM FOR THE DISTRIBUTION**

The probability of a given succession of states can again be expressed in terms of the dissipation function, by means of an auxiliary functional defined for "fluctuation paths." With the convention (1-2), the formula is outwardly the same as for the case without inertia, but of course the terms now have different meanings. The important difference is that a state  $\Gamma$  is now specified by the values of all the  $\alpha$ 's and all the  $\dot{\alpha}$ 's. If we begin, as in I, with the two-gate conditional p.d.f., we shall omit any synthetic proof, and assert that it is given by

$$f_{2n} \left( \begin{matrix} \Gamma^{(2)} \\ t_2 \end{matrix} \middle| \begin{matrix} \Gamma^{(1)} \\ t_1 \end{matrix} \right) \propto \exp \left\{ -\frac{1}{4k} \left( \int_{t_1}^{t_2} [2\Phi(\dot{\alpha}, \dot{\alpha}) + 2\Psi(\xi, \xi) - 2\dot{S}] dt \right) \right\}_{\min},$$

subject to  $\Gamma(t_1) = \Gamma^{(1)}, \Gamma(t_2) = \Gamma^{(2)}. \tag{3-1}$

The proof will consist in showing that the formula leads to the correct (1) average regressions and (2) one-gate p.d.f. (probability density function), since these completely determine a Gaussian process. Actually, this time we must check the average regressions of both  $\alpha$ 's and  $\dot{\alpha}$ 's. But we can do this in one stroke by verifying that the equations giving the regressions are indeed the set (1-4) and have the same initial conditions.

In the case without inertia we had the simplification that the  $R$  and  $s$  matrices could be simultaneously diagonalized, giving  $n$  independent equations for the phenomenological laws, and making the entropy and dissipation functions sums of squares. Here, the three matrices  $R$ ,  $s$ , and  $m$  cannot, in general, be brought simultaneously to diagonal form, so that all the variables must be handled simultaneously.

From the equality of means and modes for Gaussian distributions, the regressions are given by the condition that (3-1) be maximum with respect to  $\Gamma^{(2)}$ . Hence,

$$\int_{t_1}^{t_2} [2\Phi(\dot{\alpha}, \dot{\alpha}) + 2\Psi(\xi, \xi) - 2\dot{S}] dt_{\min} = \min,$$

subject to  $\Gamma(t_1) = \Gamma^{(1)}, \Gamma(t_2) = \Gamma^{(2)}. \tag{3.2}$

The integrand can be written in such a way as to show its positive definiteness:

$$\begin{aligned} \mathcal{L}(\alpha, \dot{\alpha}, \ddot{\alpha}) &\equiv 2\Phi(\dot{\alpha}, \dot{\alpha}) + 2\Psi(\xi, \xi) - 2\dot{S} \\ &= (\dot{\alpha} - R^{-1}\xi)_{tr} R (\dot{\alpha} - R^{-1}\xi) \\ &= (\dot{\alpha} + R^{-1}s\alpha + R^{-1}m\ddot{\alpha})_{tr} R (\dot{\alpha} + R^{-1}s\alpha + R^{-1}m\ddot{\alpha}). \end{aligned} \tag{3-3}$$

Hence the minimum of the integral is zero, which value it takes for

$$\dot{\alpha} - R^{-1}\xi = 0, \tag{3-4}$$

or

$$m\ddot{\alpha} + R\dot{\alpha} + s\alpha = 0, \tag{3-5}$$

which was to be shown. As the initial conditions [ $\Gamma(t_1) = \Gamma^{(1)}$ ] also agree, (3-1) is seen to give the right regressions.

The unconditional one-gate distribution will be correct if

$$\int_{-\infty}^{t_2} \mathcal{L}(\alpha, \dot{\alpha}, \ddot{\alpha}) dt_{\min} = S(\Gamma^{(2)}) + \text{const.} \tag{3-6}$$

subject to  $\Gamma(-\infty) = \Gamma^0 = \text{equilibrium}, \Gamma(t_2) = \Gamma^{(2)}$ .

The equations for an extreme value of the integral are

$$\frac{d^2}{dt^2} \frac{\partial \mathcal{L}}{\partial \ddot{\alpha}_i} - \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\alpha}_i} + \frac{\partial \mathcal{L}}{\partial \alpha_i} = 0, \quad i = 1 \dots n. \tag{3-7}$$

If we use 3-3, these are factorable, i.e., in matrix notation,

$$(D1 + R^{-1}s + D^2R^{-1}m)(D1 - R^{-1}s - D^2R^{-1}m)\alpha = 0, \tag{3-8}$$

where  $D = d/dt$  and  $1 = \text{unit matrix}$ .

The solutions of this equation are superpositions of the solutions of the equations obtained from the factors,

$$(D1+R^{-1}s+D^2R^{-1}m)\alpha=0, \tag{3-9}$$

$$(D1-R^{-1}s-D^2R^{-1}m)\alpha=0. \tag{3-10}$$

(3-9) is the operational form of the phenomenological equations (1-4), while (3-10) can be obtained from these by changing the sign of  $t$ . Invoking the initial condition  $\Gamma(-\infty)=\Gamma^0$ , i.e.,  $\alpha=0, \dot{\alpha}=0$  at  $t=-\infty$ , (3-9) can have only the trivial (zero) solution, for we see from (2-16),

$$\dot{S}=2\Phi(\dot{\alpha}, \dot{\alpha}),$$

that the entropy cannot decrease when the variables obey the phenomenological equations. But the entropy already has its maximum value  $S_0$  at  $t=-\infty$ , hence all but the trivial solution of (3-9) are excluded. Thus the permitted solutions of (3-8) are solutions of (3-10) [the mirror images of solutions of (3-9)].

We use (3-10) and form the quadratic form,

$$(\dot{\alpha}-R^{-1}s\ddot{\alpha}-R^{-1}m\ddot{\alpha})_t R(\dot{\alpha}-R^{-1}s\dot{\alpha}-R^{-1}m\ddot{\alpha})=0. \tag{3-11}$$

If we multiply it out and recall the definition of the thermodynamic force  $\xi$ (1-2), we have

$$2\Phi(\dot{\alpha}, \dot{\alpha})+2\Psi(\xi, \xi)+2\dot{S}=0,$$

whence

$$\mathcal{L}\equiv 2\Phi+2\Psi-2\dot{S}=-4\dot{S}. \tag{3-12}$$

Integrating  $\dot{S}$  over time then gives (3-6). We have shown that (3-1) leads to the correct average regressions and the correct one-gate p.d.f.; it is therefore the correct conditional two-gate p.d.f.

The joint p.d.f. for any number of gates can then be found by the same argument as in I. We have

$$f_{2pn} \left( \begin{matrix} \Gamma^{(1)} & \Gamma^{(2)} & \dots & \Gamma^{(p)} \\ t_1 & t_2 & & t_p \end{matrix} \right) \propto \exp \left\{ -\frac{1}{4} \frac{1}{k} \left( \int_{-\infty}^{\infty} [2\Phi(\dot{\alpha}, \dot{\alpha})+2\Psi(\xi, \xi)] dt \right)_{\min} \right\}, \tag{3-13}$$

subject to  $\Gamma(t_1)=\Gamma^{(1)}, \Gamma(t_2)=\Gamma^{(2)}, \dots, \Gamma(t_p)=\Gamma^{(p)}$ .

Since the path (now given by  $\alpha$  and  $\dot{\alpha}$ ) can be specified to any desired degree of precision (any number of gates), we have again obtained a probability *functional* for fluctuations, in terms of the dissipation function for irreversible processes.

The statement made in I, that the formula is still valid when the state is incompletely specified in one or more gates, is true here as well, and for the same reason: the p.d.f. is Gaussian in all the variables, hence integration over one variable is equivalent to taking the minimum of the integral with respect to that variable. Such a statement is, indeed, necessary in order that (3-13) have a nontrivial meaning when either the  $s$  or the  $m$  matrix is not positive definite; for in this case the system does not really have  $2n$  degrees of freedom. The matrices may be, at worst, positive semidefinite, by the Second Law. The matrix  $m$  will certainly be semidefinite when an  $\alpha$  variable appears in the entropy function and the corresponding  $\dot{\alpha}$  does not. In fact, if all the  $m_{ij}$  become zero, (3-13) must reduce to the formula in I (4-23) when we integrate out all the  $\dot{\alpha}$  variables, which indeed we must in order to have non-zero probabilities. The  $s$  matrix will be semidefinite whenever an  $\dot{\alpha}$  variable appears in the entropy function and the corresponding  $\alpha$  does not. We have two distinct types of examples of such systems: for a Brownian particle in an infinite (field-free) medium, its position does not enter the entropy function, but its velocity does. Any nontrivial specification of the position leads to zero probability. On the other hand, for an inductive series circuit without capacitance, specification of the electric charge is quite meaningless, although its rate of change, the current, enters the entropy function.

It may be noticed that the roles of the functions  $\Phi(\dot{\alpha}, \dot{\alpha})$  and  $\Psi(\xi, \xi)$  in this paper have changed from those in I. For the systems without kinetic energy of I, the thermodynamic forces  $X_i=\partial S/\partial\alpha_i$  are functions of the state  $\Gamma$ . Hence  $\Psi(X, X)$  is a function of the state, while  $\Phi(\dot{\alpha}, \dot{\alpha})$  depends on its change in time. For the systems with kinetic energy considered here, the  $\dot{\alpha}$ 's belong to the description of the state  $\Gamma$ . On the other hand, the thermodynamic forces  $\xi_i=\partial S/\partial\alpha_i+(d/dt)\times(\partial S/\partial\dot{\alpha}_i)$  are not functions of the state alone. Hence  $\Phi(\dot{\alpha}, \dot{\alpha})$  is a function of the state alone, and  $\Psi(\xi, \xi)$  depends on its rate of change in time.

The authors wish to express their appreciation of the friendly hospitality of the Royal Society Mond Laboratory, University of Cambridge, England, during the academic year 1951-1952. Moreover, they gratefully acknowledge a U. S. Atomic Energy Commission Pre-doctoral Fellowship held by S.M., and a U. S. Government Grant under the Fulbright Act to L.O., which made their stay in Cambridge possible.