

Network theory of microscopic and macroscopic behavior of master equation systems

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A general microscopic and macroscopic theory is developed for systems which are governed by a (linear) master equation. The theory is based on a network representation of the master equation, and the results are obtained mostly by application of some basic theorems of mathematical graph theory. In the microscopic part of the theory, the construction of a steady state solution of the master equation in terms of graph theoretical elements is described (Kirchhoff's theorem), and it is shown that the master equation satisfies a global asymptotic Liapunov stability criterion with respect to this state. The Glandsdorff-Prigogine criterion turns out to be the differential version and thus a special case of the global criterion. In the macroscopic part of the theory, a general prescription is given describing macrostates of the systems arbitrarily far from equilibrium in the language of generalized forces and fluxes of nonlinear irreversible thermodynamics. As a particular result, Onsager's reciprocity relations for the phenomenological coefficients are obtained as coinciding with the reciprocity relations of a near-to-equilibrium network.

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I. INTRODUCTION

A frequent situation of nonequilibrium physics is a system S in contact with several different reservoir systems for thermal energy, volume, matter, electric charge, etc. Examples are: a rod of a heat conducting material with different fixed temperatures at its ends, a permeable or semipermeable membrane between two different electrolyte solutions, or a system of coupled chemical reactions where some of the reactants are continuously fed into the system and others are continuously withdrawn. In all these cases, the reservoir systems are not necessarily in mutual equilibrium such that the system S cannot also achieve an equilibrium state, but at most tend into some nonequilibrium steady state. The purpose of this article is to review some of the mathematical and physical techniques which have turned out to yield appropriate descriptions of such nonequilibrium situations. The starting point of all these techniques is a master equation formulation of the system S , i.e., an equation

$$\frac{d}{dt}p_i(t) = \sum_{j=1}^N \{ \langle i|j \rangle p_j(t) - \langle j|i \rangle p_i(t) \} \quad (1.1)$$

for the dynamical evolution of a probability distribution $p_i(t)$ over states $i=1,2,\dots,N$ which characterize the system S . The quantity $\langle i|j \rangle$ is the transition probability per time to state i from state j . It contains internal rate constants as well as external conditions imposed by the coupling to the reservoir systems like differences of temperature, pressure, and electrochemical potentials between the different reservoir systems. Regarding the nature of the states $i=1,2,\dots,N$ these could be chosen such as to represent a complete quantum-mechanical or classical description of the system S . In most cases of interest, however, the states $i=1,2,\dots,N$ will be the result of some coarse graining procedure and thus each already involving a large number of quantum-mechanical or classical degrees of freedom. In any case, we shall call the description of S in terms of the states $i=1,2,\dots,N$ a microscopic description as to be distinguished from a macroscopic description which will be introduced later. Let us also mention that the number N of states need not be finite. In all following considerations, the limit $N \rightarrow \infty$ can be performed without principal difficulties. Examples for the master equation (1.1) and the appropriate choice of states will be given in Sec. II.

The techniques which we will be presenting in the following sections will all amount to a mathematical and physical analysis of the master equation (1.1). According to the preliminary distinction between a microscopic and a macroscopic description of the nonequilibrium system S , this analysis involves two corresponding parts. In the microscopic part, we shall investigate problems like the existence and construction of steady state solutions of (1.1) (Sec. III), mathematical properties of time-dependent solutions (Sec. IV), stability of time-dependent solutions in the "physical region," i.e., the region where

$$0 \leq p_i(t) \leq 1, \quad \sum_{i=1}^N p_i(t) = 1 \quad (1.2)$$

(Sec. V), overall stability and the uniqueness of the steady state solution (Sec. VI), and eventually the role of the Glandsdorff-Prigogine criterion of stability. In con-

trast to the microscopic description of the system in terms of probability distributions $\{p_i\}$ for the microscopic states $i=1, 2, \dots, N$, the phenomenological theory of nonequilibrium thermodynamics defines macro-states by assigning values to a set of independent macroscopic forces or fluxes. In the macroscopic part of our analysis, we shall establish the relationship between the master equation (1.1) and the macroscopic variables, forces and fluxes, on the basis of a graph or network representation of the system of equations (1.1). The basic concepts and facts from graph theory which are needed for this procedure will be represented in Sec. VIII. In Sec. IX, the macroscopic properties of the steady state, in particular the macroscopic entropy production, will be discussed.

Up to this point, all investigations and all results obtained apply to thermodynamic states which may be arbitrarily far from thermal equilibrium. In Sec. X, however, we shall focus our interest on the thermal equilibrium and on its vicinity, the so-called linear range of irreversible thermodynamics. The main results of this section include the derivation of the linear relationship between macroscopic forces and fluxes and the proof of Onsager's reciprocity relation for the phenomenological coefficients. As pointed out above, we shall make use of some elementary concepts and facts of graph theory, particularly in Secs. III and VIII. Although we try to represent the mathematical background as far as possible, we refer for further details to the monographs of Ore (1962), Desoer, Kuh (1969) and Chen (1971).

II. MASTER EQUATION DESCRIPTION: TWO EXAMPLES

A. Pores in a membrane

Our first example of a master equation description of a nonequilibrium system was originally initiated by a biophysical problem. It is a common physiological observation that cell membranes, i.e., the walls of a biological cell, separate two electrolyte solutions which are usually very different in their chemical composition. In many cases, the cell membranes are permeable very selectively to particular kinds of ions like Na^+ or K^+ . The large difference in the composition of the adjoining solution means that the membrane is in a very pronounced nonequilibrium situation as typical for many biological systems. To account for the selectivity of transport, one has developed the model concept of a very narrow membrane pore as a transport channel for particular kinds of ions or molecules. Such a pore is envisaged as a one-dimensional array of $N-1$ stable sites for exactly that kind of ions or molecules. It traverses the membrane perpendicular to the membrane plane and connects the two solutions as indicated in part (a) of Fig. 1.

Let us focus our interest upon the case of an ion permeating through the pore. Assuming that electrostatic repulsion prevents situations with more than one ion occupying the pore, it can exist in N states: $i=1, \dots, N-1$ for occupation of the $N-1$ sites, and the state $i=N$ for the empty pore. Obviously, we can represent this model by a diagram or graph by assigning nodes or vertices to each of the states, and by connecting lines or edges to the allowed transitions between the states. In the case

of our simple example, the representative graph is a cycle shown in part (b) of Fig. 1. The edges or transitions stand for elementary diffusion jumps of the ion between neighboring sites or into or out of the pore. The transition probabilities per time including an applied electric field are given by

$$\begin{aligned} \langle i+1 | i \rangle &= k_i e^\phi \quad i=1, 2, \dots, N-1, \\ \langle i | i+1 \rangle &= k_i e^{-\phi} \quad i=N, 1, \dots, N-2, \\ \langle 1 | N \rangle &= c k_N e^\phi, \quad \langle N-1 | N \rangle = c' k_{N-1} e^{-\phi}, \\ \phi &= z e F \Delta / 2 N k_B T, \end{aligned} \quad (2.1)$$

where c, c' = ionic concentrations on the left and right respectively, F = applied electric field ($F > 0$ from left to right), e = elementary charge, z = ionic valency, k_B = Boltzmann's constant, T = temperature, Δ = membrane thickness, k_i = internal rate constants. In (2.1), a cyclic numbering has been adopted: $N+1 \hat{=} 1$. Note that in the representative diagram a vertex represents one micro-state with its probability p_i , but an edge represents two transition probabilities $\langle i | j \rangle$ and $\langle j | i \rangle$, one for each of the two possible directions of the transition.

The diagrammatic representation that we just described in the case of our simple example is a very general and helpful technique for studying models of higher complexity. As Hill and Plesner (1965) have shown, quite a variety of rather complex model systems are covered by the master equation (1.1). Examples particularly for membrane models have been given by Hill and Kedem (1966) and Hill (1968). The reason why such a diagrammatic technique is needed even though the underlying mathematical equation (1.1) is linear, lies in the fact that the linearity does indeed guarantee a lot of theorems on the existence of solutions, but does not help any further if one asks for the solution of particular models, for the asymptotic behavior and stability of solutions, or for the thermodynamic description of the model systems.

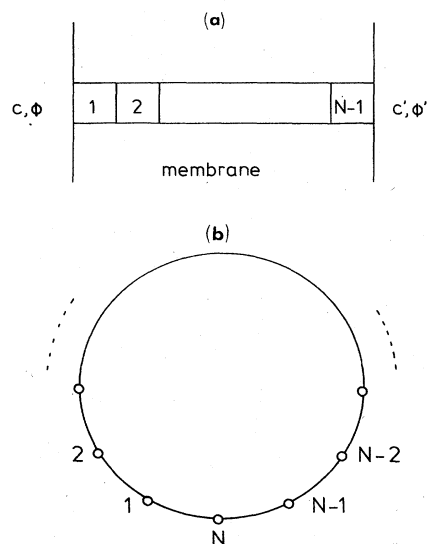


FIG. 1. (a) Simple membrane pore model, (b) diagram of states of the model.

B. Autocatalytic reaction system

Our second example is a system of two chemical reactions



In this system, the concentration x of the molecules of type X is variable, whereas that of the molecules A , B , and C is kept fixed by coupling the system to appropriate reservoir systems. The deterministic theory of the system (2.2) starts from the rate equation for the concentration x which is obtained from (2.2) as

$$dx/dt = k_1 a x^2 - k'_1 x^3 - k_2 b x + k'_2 c, \quad (2.3)$$

where a, b, c are the fixed concentrations of A, B , and C , and k_1, k'_1, k_2, k'_2 are the forward and reverse rate constants of the reactions (1) and (2) in (2.2), respectively. Schlögl (1972) has investigated the deterministic properties of this system. It shows instabilities of the type of multiple steady states and represents a simple model for a first-order nonequilibrium phase transition.

Whereas in our first example we could construct the probabilities p_i in the master equation as $p_i = X_i/X$ where X_i is the number of pores in the state i , and X is the total number of pores, such a construction is impossible for the present example since the deterministic rate equation (2.3) is nonlinear. Instead, one has to introduce a probability $p(X, t)$ that the system contains the number X of molecules of the type X at time t . (In order to avoid too many notations, we choose the symbol X also for the number of molecules of type X). Now the variable X replaces the subscripts i which denote the states of the system in the distribution $\{p_i\}$. An expression for the time derivative of $p(X, t)$ is then obtained by taking into account all reaction transitions from states with numbers $X+1$ and $X-1$ to the state with a number X of molecules of type X and vice versa. As discussed by Janssen (1974) in detail, the resulting master equation reads

$$\begin{aligned} \frac{d}{dt} p(X, t) = \sum_{\rho=1}^2 \{ \langle X | X-1 \rangle^{(\rho)} p(X-1, t) + \langle X | X+1 \rangle^{(\rho)} p(X+1, t) \\ - [\langle X-1 | X \rangle^{(\rho)} + \langle X+1 | X \rangle^{(\rho)}] p(X, t) \}. \end{aligned} \quad (2.4)$$

The superscript $\rho=1, 2$ refers to the two reactions which may each increase or decrease the number X by unity. The transition probabilities are

$$\langle X | X-1 \rangle^{(1)} = k_1 a (X-1)(X-2)/V, \quad \langle X | X-1 \rangle^{(2)} = k'_2 c V \quad (2.5)$$

$$\langle X-1 | X \rangle^{(1)} = k'_1 X(X-1)(X-2)/V^2, \quad \langle X-1 | X \rangle^{(2)} = k_2 b X$$

and V is the volume of the system.

Following the same translation rules as in the case of the first example we again represent the master equation (2.4) by a diagram or basic graph which is shown in Fig. 2. From this graph we learn that there may be several transitions between the same pair of states. In our example, these transitions belong to independent chemical reactions and thus have to be treated independently in the mathematical and physical considerations in subsequent

sections. We stress this point because for the purpose of a solution of (2.4) [Landauer (1962), Haken (1974, 1975), Janssen (1974)] it is convenient to compress the two transitions formally into one. This is a purely formal trick and must not be misinterpreted as a physical change of the system. We will come back to this point later.

III. STEADY STATE SOLUTION

For our following investigations let us adopt a very general point of view. Given any physical system which is described by a master equation (1.1), we first construct its basic graph G as pointed out in Sec. II. Our general results will not depend on the particular nature of the system. We shall refer to the examples given in Section II only to illustrate the results. An essential prerequisite for the investigations in this paper is the assumption that if there exists a transition from some state j to some state i , i.e., $\langle i | j \rangle > 0$, then the reverse transition is also possible, i.e., $\langle j | i \rangle > 0$. The reason for this assumption is first of all the fact that for a real transition between physical states there will always exist, at least in principle, the opposite transition, possibly at a very low rate. Moreover, it is convenient for mathematical purposes to start with the above assumption and to discuss the limit of vanishing transition rates for single directions only in the final results. We shall perform such limits in the steady state solution for two typical examples at the end of the section.

With the above assumption that $\langle i | j \rangle > 0$ implies $\langle j | i \rangle > 0$, we may now assume without any loss of generality that our basic graph G is connected in the sense that to each pair of states or vertices (i, j) , $i \neq j$, there exists at least one sequence of transitions or edges connecting them in both directions. If G were not connected, the physical system behind G would decompose into noninteracting subsystems which could be treated separately.

To obtain the steady state solution \bar{p}_i of (1.1), i.e., $d\bar{p}_i/dt = 0$ (not to be confused with the thermodynamic equilibrium) one would have to solve the linear equation

$$\sum_j W_{ij} \bar{p}_j = 0, \quad (3.1)$$

where

$$W_{ij} = \langle i | j \rangle - \delta_{ij} \sum_k \langle k | i \rangle \quad (3.2)$$

is an $N \times N$ matrix if N is the total number of states, $i = 1, 2, \dots, N$, as before. The existence of a nontrivial solution of (3.1) is guaranteed if

$$\det \{W_{ij}\} = 0 \quad (3.3)$$

which follows from

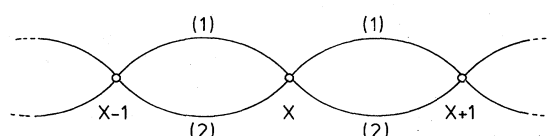


FIG. 2. Graph of the master equation description of the autocatalytic reaction system.

$$\sum_i W_{ij} = \sum_i \left(\langle i|j \rangle - \delta_{ij} \sum_k \langle k|i \rangle \right) = 0. \quad (3.4)$$

Equation (3.3) means that the rank $r\{W_{ij}\}$ of W_{ij} is less than N

$$r\{W_{ij}\} \leq N - 1. \quad (3.5)$$

The theory of linear equations does not tell us whether at least one nontrivial solution of (3.1), if normalized to 1,

$$\sum_i \bar{p}_i = 1 \quad (3.6)$$

satisfies the condition

$$0 \leq \bar{p}_i \leq 1 \quad (3.7)$$

which should be required to interpret the $\{p_i\}$ as a probability distribution. Moreover, it is not at all trivial to answer the following questions: how many nontrivial solutions of (3.1) exist, and how many of them can be submitted to the conditions (3.6) and (3.7)? Even if we know that only one simultaneous solution of (3.1) and (3.6) exists, its analytical expression obtained from usual linear algebra in terms of determinants and subdeterminants (Cramer's rule) is not tractable for a discussion of the properties of the steady state in particular systems.

The diagrammatic representation of a system by its basic graph G has led to an operative and very elegant method to construct the steady state solution \bar{p}_i in terms of partial graphs of G . Moreover, the \bar{p}_i obtained in this way automatically satisfies (3.6) and (3.7). We shall briefly review this method without proof. A detailed description and proof including application to models like that of our example was given by Hill (1966). Before Hill, other authors [Bott, Mayberry (1954), King, Altman (1956)] had already made use of this method, the first one being Kirchhoff in 1847 in context with network theory. We shall therefore refer to it as to Kirchhoff's theorem.

Let us start by defining a maximal tree $T(G)$ of our basic graph G . $T(G)$ is uniquely characterized by the following properties:

- (1) $T(G)$ is a covering subgraph of G , i.e., (a) all edges of $T(G)$ are edges of G , and (b) $T(G)$ contains all vertices of G ;
- (2) $T(G)$ is connected;
- (3) $T(G)$ contains no circuits (cyclic sequences of edges). It is easily shown, that $T(G)$ has $N - 1$ edges if N is the number of states and thus of vertices in G , or with other words, $\nu = E - N + 1$ edges of G are missing in $T(G)$ where E is the number of edges in G .

Part (b) of Fig. 3 shows all possible maximal trees $T(G)$ of the graph G defined in part (a).

Let us denote the various possible maximal trees by $T^{(\mu)}(G)$, $\mu = 1, 2, \dots, M$. The total number M of maximal trees crucially depends on the topological structure of G and on its number E of edges. For the example in Fig. 3(a), (b) we have $M = 8$, for the simple cycle in Fig. 1(b), $M = E = N$. If G consists of two cycles which are connected in one vertex, $M = E_1 E_2$, where E_1 and E_2 are

the numbers of edges in the two cycles. If the two cycles have one edge in common instead of one vertex and E_1 and E_2 are the numbers of their separate edges, then $M = E_1 \cdot E_2 + E_1 + E_2$.

From each of the maximal trees $T^{(\mu)}(G)$ we obtain its i -directed version $T_i^{(\mu)}(G)$ by directing all edges of $T^{(\mu)}(G)$ toward the vertex with number i . This is a unique procedure for every $T^{(\mu)}(G)$ and every i , since the $T^{(\mu)}(G)$ contain no cycles and cover all vertices of G . Part (c) of Fig. 3 shows all i -directed version $T_i^{(\mu)}(G)$ for $i = 1$ in that example.

To every $T_i^{(\mu)}(G)$ we assign an algebraic value $A(T_i^{(\mu)}(G))$ by multiplying all transition probabilities $\langle i|j \rangle$ whose edges occur in $T_i^{(\mu)}(G)$ in the direction to i from j . For example, to the first one of the 1-directed $T_1^{(\mu)}(G)$ in Fig. 3(c) the product $\langle 1|2 \rangle \langle 2|3 \rangle \langle 3|4 \rangle$ would be assigned. Kirchhoff's theorem now states that the steady state solution \bar{p}_i is given by

$$\bar{p}_i = S_i / S, \quad (3.8)$$

where

$$S_i = \sum_{\mu=1}^M A(T_i^{(\mu)}(G)), \quad S = \sum_{i=1}^N S_i \quad (3.9)$$

(N being the number of vertices in G). From (3.8) and (3.9) we immediately derive the normalization condition (3.6). Since all $S_i > 0$, none of the \bar{p}_i can vanish and thus none of them can be equal to 1 and hence

$$0 < \bar{p}_i < 1, \quad (3.10)$$

i.e., the equality signs in (3.7) can be excluded for the

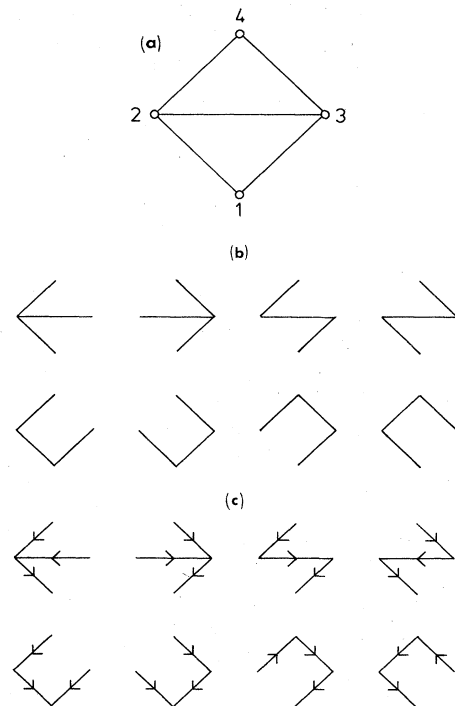


FIG. 3. Example for constructing maximal trees and its directed versions: (a) basic graph G , (b) all possible maximal trees $T^{(\mu)}(G)$ of G , (c) 1-directed versions $T_1^{(\mu)}(G)$ of the maximal trees.

steady state.

Let us now discuss what could happen if transition rates vanish for a single direction but remain finite in the reverse direction. It is easily visualized that such a situation may drastically reduce the number of terms contributing to S_i in Eq. (3.9). Let us consider two examples. In the first example we assume that a transition rate for a single direction vanishes along a bridge of G . A bridge is defined as a sequence of edges which is not part of any cycle of G . Thus cutting an edge along a bridge means to cut G into two pieces. An example for a bridge is shown in Fig. 4(a). If now along such a bridge we have $\langle i|j\rangle=0$ but $\langle j|i\rangle>0$, we immediately see from Kirchhoff's theorem that the steady state probabilities of all states on the i side of the bridge vanish since their values of $A(T_i^{(\mu)}(G))$ necessarily contain the factor $\langle i|j\rangle$. For the calculation of the remaining probabilities on the j side of the bridge we may reduce the original graph G to the partial graph G' containing all vertices on the j side since their values of $A(T_j^{(\mu)}(G))$ have a common factor made up from transition rates on the i side which is canceled when taking the ratio in Eq. (3.8). For the second example let us assume that in the cycle of Fig. 1 we have $\langle N-1|N\rangle=0$ but $\langle N|N-1\rangle>0$. Let $T^{(\mu)}(G)$ be the maximal tree obtained from the cycle G by omitting the edge between the vertices $\mu-1$ and μ , where $\mu=1, 2, \dots, N$ and $\mu=0$ is equivalent to $\mu=N$. We then immediately see that $A(T_i^{(\mu)}(G))=0$ for $\mu=1, 2, \dots, i$ such that the evaluation of S_i is reduced to

$$S_i = \sum_{\mu=i+1}^N A(T_i^{(\mu)}(G)). \quad (3.11)$$

The answer to the question, whether Kirchhoff's theorem is of any use for the evaluation of actual systems, primarily depends on the topological structure of G , but only secondarily on the number of vertices of G .

First of all, there are the cases where G is a simple finite or infinite chain of states. In such a case, the Kirchhoff solution coincides with the solution of the master equation given by Landauer (1962) and Haken (1974, 1975). This even applies to cases where G is a chain of cycles as in the second example of Sec. II, cf., Fig. 2. The reader may easily verify that in this case the expression S_X as defined by (3.9) for $i=X$ is given as

$$S_X = \prod_{\xi=1}^X (\langle \xi | \xi - 1 \rangle^{(1)} + \langle \xi | \xi - 1 \rangle^{(2)}) \times \prod_{\xi=X}^{\infty} (\langle \xi | \xi + 1 \rangle^{(1)} + \langle \xi | \xi + 1 \rangle^{(2)}) \quad (3.12)$$

Equation (3.12) illustrates the meaning of compressing different transitions into one as a formal trick to solve the steady state master equation. Defining

$$\langle \xi | \xi' \rangle = \langle \xi | \xi' \rangle^{(1)} + \langle \xi | \xi' \rangle^{(2)} \quad (3.13)$$

reduces the chain of cycles to a chain of states as far as the formal structure of the steady state solution is concerned. Insertion of (3.12) into (3.8) directly leads to the solutions as described by Landauer and Haken.

For less symmetric structures of G the application of Kirchhoff's theorem requires a little more of graph theoretical or combinatorial analysis. If G consists of a

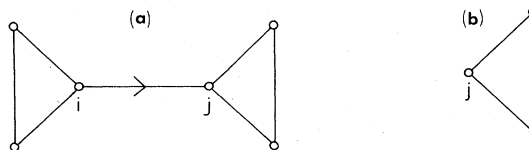


FIG. 4. (a) Graph with a bridge between the states i and j , the arrow indicating $\langle i|j\rangle=0$, (b) reduced graph G' for the steady state solution.

number of up to three or four cycles which are connected by common vertices or edges, the combinatorial problem of finding all maximal trees may be solved analytically. Examples of this type may be found in the paper by Hill and Kedem (1966) or even for arbitrary large numbers of vertices in an earlier paper by the author [Schnakenberg (1973)]. Apart from analytic methods, Heckmann *et al.* (1969) have developed a general algorithm for a computer evaluation of arbitrary complex systems on the basis of Kirchhoff's theorem. It is evident that the computing time for this algorithm again strictly depends on the topological structure of G .

IV. PROPERTIES OF THE TIME-DEPENDENT SOLUTION

From the theory of systems of ordinary differential equations with constant coefficients we know that for every set of initial conditions

$$p_i(t_0) = p_i^0, \quad i=1, 2, \dots, N \quad (4.1)$$

there exists a unique solution $p_i(t)$ of the master equation (1.1) satisfying the initial condition (4.1) and being analytic for all finite values of t . Furthermore, we derive from (1.1)

$$\frac{d}{dt} \sum_i p_i(t) = \sum_j \left(\sum_i W_{ij} \right) p_j(t) = 0 \quad (4.2)$$

by making use of (3.4). Thus, the sum of the $p_i(t)$ is a constant of motion. If we normalize the initial values p_i^0 ,

$$\sum_i p_i^0 = 1, \quad (4.3)$$

the corresponding solution $p_i(t)$ satisfying (4.1) remains normalized

$$\sum_i p_i(t) = 1. \quad (4.4)$$

In order to interpret the $p_i(t)$ as a probability distribution, we still have to prove that in addition to (4.4)

$$0 \leq p_i(t) \leq 1 \quad (4.5)$$

for all t . In fact, we shall be able to prove $p_i(t) > 0$ for all t and i , if $p_i(t)$ satisfies the initial conditions (4.1), if the p_i^0 are subject to (4.3), if

$$0 \leq p_i^0 \leq 1, \quad (4.6)$$

and if the representative graph G of the system is connected. From $p_i(t) > 0$ together with (4.4) we then conclude that (4.5) holds even without the equality signs.

Our findings will be in complete agreement with that of Keizer (1972) obtained by application of methods from matrix theory to the master equation (1.1).

Under the above assumptions, we first prove that there exists a $\tau > 0$ such that for all t within the interval $t_0 < t < t_0 + \tau$, $p_i(t) > 0$ for all i . If all $p_i^0 > 0$, the existence of a τ as stated above is evident. Therefore assume that for some i , $p_i(t_0) = p_i^0 = 0$ such that the master equation (1.1) gives

$$\dot{p}_i(t_0) = \left(\frac{d}{dt} p_i(t) \right)_{t=t_0} = \sum_j \langle i | j \rangle p_j(t_0). \quad (4.7)$$

If at least for one of the neighbors j of i , i.e., for at least one vertex $j \neq i$ with $\langle i | j \rangle \neq 0$ (j being directly connected to i by a single edge in G) $p_j(t_0) = p_j^0 > 0$, then Eq. (4.7) yields $\dot{p}_i(t_0) > 0$. If for all neighbors j of i , $p_j(t_0) = p_j^0 = 0$ and thus $\dot{p}_i(t_0) = 0$, we take the second time derivative of the master equation (1.1) to obtain

$$\ddot{p}_i(t) = \frac{d^2}{dt^2} p_i(t) = \sum_j [\langle i | j \rangle \dot{p}_j(t) - \langle j | i \rangle \dot{p}_i(t)]. \quad (4.8)$$

Inserting $p_i(t_0) = 0$, $\dot{p}_i(t_0) = 0$ for $t = t_0$ into (4.8), and expressing $\dot{p}_j(t_0)$ again by the master equation (1.1), we get for $p_j(t_0) = 0$

$$\ddot{p}_i(t_0) = \sum_{j,k} \langle i | j \rangle \langle j | k \rangle p_k(t_0). \quad (4.9)$$

In Eq. (4.9), the vertex i is linked to its second order neighbors k in G . If at least for one of those $p_k(t_0) = p_k^0 > 0$, then Eq. (3.9) yields $\ddot{p}_i(t_0) > 0$; otherwise $\ddot{p}_i(t_0) = 0$. In the latter case, we continue this procedure until in a connected graph G we must arrive eventually at a positive ν -th-order time derivative of $p_i(t)$ at $t = t_0$. This then ensures the existence of a τ_i such that $p_i(t) > 0$ for $t_0 < t < t_0 + \tau_i$, and consequently $p_i(t) > 0$ for $t_0 < t < t_0 + \tau$ and all $i = 1, 2, \dots, N$ with $\tau = \min(\tau_i)$. In the second and final step we show that it can never happen for $t > t_0$ that any of the $p_i(t)$ vanishes. Let us assume the contrary and let $t_1 > t_0$ be the first time that any of the $p_i(t)$ vanishes: $p_i(t_1) = 0$. In the same way as in Eq. (4.7) we get

$$\dot{p}_i(t_1) = \sum_j \langle i | j \rangle p_j(t_1). \quad (4.10)$$

Again we have two possibilities:

(a) either for at least one of the neighbors j of i $p_j(t_1) > 0$ and thus $\dot{p}_i(t_1) > 0$, i.e., $p_i(t)$ has a first-order zero for $t = t_1$ and $p_i(t)$ would yield negative values for $t < t_1$ sufficiently near to t_1 . This is a contradiction, since t_1 was assumed to be the first time that any of the $p_i(t)$ vanishes.

(b) or for all neighbors j of i is $p_j(t_1) = 0$. In this case, we apply (4.10) to the neighbors j of i to see if one of the $\dot{p}_j(t_1) > 0$ and so on. In a connected graph, we eventually must arrive at a $\dot{p}_k(t_1) > 0$ since not all of the $p_i(t_1)$ can vanish, this following from (4.4) for $t = t_1$. If now $\dot{p}_k(t_1) > 0$ and $p_k(t_1) = 0$ we return to case (a).

V. LIAPUNOV STABILITY

In this section, we shall prove that the master equation (1.1) is stable whenever the initial conditions satisfy

(4.3) and (4.6). For this purpose, we make use of a stability theorem which was proposed by Schlögl (1971). Let

$$\dot{x}_i = F_i(x_1, \dots, x_n), \quad i = 1, 2, \dots, n \quad (5.1)$$

be a system of differential equations for the functions $x_i(t)$, let A be a region in the $\mathbf{x} = (x_1, \dots, x_n)$ -space which contains the origin $\mathbf{x} = 0$, and let $K(\mathbf{x})$ be a function defined in A and having the following properties:

- (a) $K(\mathbf{x})$ has continuous second-order derivatives in A
- (b) $K(\mathbf{x}) \geq 0$ in A (5.2)

the equality sign being valid for $\mathbf{x} = 0$ only,

- (c) $K(\mathbf{x})$ is concave, i.e.,

$$\sum_{i,j} \frac{\partial^2 K}{\partial x_i \partial x_j} \delta x_i \delta x_j > 0 \quad (5.3)$$

for all \mathbf{x} in A and $\delta \mathbf{x} \neq 0$,

$$\begin{aligned} \text{(d)} \quad \frac{dK}{dt} &= \sum_i \frac{\partial K(\mathbf{x})}{\partial x_i} \dot{x}_i \\ &= \sum_i \frac{\partial K(\mathbf{x})}{\partial x_i} F_i(\mathbf{x}) \leq 0 \end{aligned} \quad (5.4)$$

the equality sign being valid for $\mathbf{x} = 0$ only.

Properties (b) and (c) imply that there exists a closed surface $S(C)$: $K(\mathbf{x}) = C$ ($C > 0$) within A such that $S(C)$ encloses all surfaces $S(C')$ with $C > C' > 0$. Let \bar{A} be the interior of the surface $S(C)$ with maximal C such that $S(C)$ is still contained in A . Then the stability theorem states that any solution of (5.1) starting in \bar{A} remains in \bar{A} and tends into the origin at $t \rightarrow \infty$:

$$\lim_{t \rightarrow \infty} x_i(t) = 0 \quad \text{for all } i. \quad (5.5)$$

The proof of this theorem is almost evident. It may be regarded as "strong version" of Liapunov's stability criterion which, in its usual form, makes less incisive assumptions [Lasalle, Lefschetz (1961)]. On the other hand, the strong version ensures stability in a whole region \bar{A} and not only in the vicinity of the origin.

When applying the above stability theorem to the master equation (1.1) we follow the work of Schlögl (1971) and choose an arbitrary linear parametrization for the probabilities p_i ,

$$p_i = \bar{p}_i + \sum_{k=1}^{N-1} U_{ik} x_k \quad (5.6)$$

such that

$$\sum_i \bar{p}_i = 1 \quad (5.7)$$

is satisfied by an appropriate choice of the U_{ik} . The region A is chosen as that part of the parameter space for which

$$0 \leq p_i \leq 1. \quad (5.8)$$

The \bar{p}_i of Eq. (5.6) are the probabilities of an arbitrary steady state in the "physical region" defined by (5.7) and (5.8). The Kirchhoff theorem ensures the existence of at least one such steady state. As Liapunov function we choose

$$K(p_1, \dots, p_N) = \sum_i p_i \log \frac{p_i}{\bar{p}_i} \quad (5.9)$$

which can be expressed in terms of the independent parameters x_i by inserting (5.6) into (5.9). The function of Eq. (5.9) was introduced by Kullback (1951 a, b) and Rényi (1966) as the gain of information when replacing the distribution $\{\bar{p}_i\}$ by a different distribution $\{p_i\}$. Based on this interpretation, Schlögl has recognized its significance as a Liapunov function for physical systems.

Properties (a), (b), and (c) are easily established [Schlögl (1971)] and moreover, it can be shown that \tilde{A} coincides with A , i.e., \tilde{A} corresponds to the whole physical region (5.7), (5.8). What remains to be demonstrated is property (d), the proof of which depends on the Markovian type of the master equation (1.1). By inserting (1.1) into \dot{K} and by making use of (4.2) we obtain

$$\begin{aligned} \frac{dK}{dt} &= \sum_i \dot{p}_i \log \frac{p_i}{\bar{p}_i} \\ &= \sum_{i,j} \langle i|j \rangle p_j \log \frac{p_i}{\bar{p}_i} - \sum_{i,k} \langle k|i \rangle p_i \log \frac{p_i}{\bar{p}_i} \\ &= \sum_{i,j} \langle i|j \rangle p_j \log \frac{p_i \bar{p}_j}{\bar{p}_i p_j} \\ &= \sum_{i,j} \langle i|j \rangle p_j \left(\frac{p_i \bar{p}_j}{\bar{p}_i p_j} - 1 \right) \end{aligned} \quad (5.10)$$

since $\log x \leq x - 1$ for $x > 0$, and $\langle i|j \rangle p_j > 0$. In the last expression of (5.10), $\langle i|j \rangle$ can be replaced by W_{ij} [c.f. Eq. (3.2)] since the diagonal terms $i=j$ do not contribute. In this way we have

$$\begin{aligned} \frac{dK}{dt} &\leq \sum_{i,j} W_{ij} p_j \left(\frac{p_i \bar{p}_j}{\bar{p}_i p_j} - 1 \right) \\ &= \sum_i \frac{p_i}{\bar{p}_i} \sum_j W_{ij} \bar{p}_j - \sum_j \left(\sum_i W_{ij} \right) p_j = 0 \end{aligned} \quad (5.11)$$

by making use of Eqs. (3.1) and (3.4). As can be seen from (5.10), the equality sign holds only if for all pairs i, j $p_i/\bar{p}_i = p_j/\bar{p}_j$ which reduces to $p_i = \bar{p}_i$ for all i .

We have shown that any solution which starts in the physical region (5.7), (5.8) is asymptotically stable with respect to any steady state in the physical region, for example that of the Kirchhoff theorem. Thus, we obtain as a by-product of our considerations that the steady state of the Kirchhoff theorem is unique in the physical region since a solution cannot be asymptotically stable with respect to different steady states.

VI. THE EIGENVALUES OF THE TRANSITION MODEL

The most general form of the solution for the system (1.1) of linear homogeneous differential equations reads

$$p_i(t) = \sum_\nu c_\nu u_i^{(\nu)} Q_i^{(\nu)}(t) e^{-\lambda_\nu t}. \quad (6.1)$$

In (6.1) the λ_ν are the eigenvalues of the matrix $-W_{ij}$ defined by (3.2) with eigenvectors $(u_1^{(\nu)}, \dots, u_N^{(\nu)})$, $\nu = 1, 2, \dots$, and the c_ν are arbitrary constants. Regarding the $Q_i^{(\nu)}(t)$, the following cases are possible:

(1) No degeneracy: all λ_ν 's are different from each other, and $Q_i^{(\nu)}(t) \equiv 1$.

(2) Degeneracy: among the λ_ν 's a group of k are equal (k -fold degeneracy).

(a) If for the k degenerate eigenvalues a number of k linear independent eigenvectors can be found, we again have $Q_i^{(\nu)}(t) \equiv 1$ for this group. In this case, we prefer to denote the degenerate λ_ν 's by different values of ν .

(b) If for the group of the k degenerate eigenvalues the number of linear independent eigenvectors is less than k , the $Q_i^{(\nu)}(t)$ are polynomials of degree less than k . In this case, we distinguish the linear independent eigenvectors by different values for ν .

We need not go into any further details since for the following considerations the general structure of the solution in (6.1) will be sufficient. The existence of the steady state in the Kirchhoff theorem implies that at least one eigenvalue λ_ν , say λ_0 , vanishes: $\lambda_0 = 0$. Denoting the Kirchhoff steady state by \bar{p}_i we may write the general solution of (1.1) in the form

$$p_i(t) = \bar{p}_i + \sum_{\nu \geq 1} c_\nu u_i^{(\nu)} Q_i^{(\nu)}(t) e^{-\lambda_\nu t} \quad (6.2)$$

since $p_i(t) - \bar{p}_i$ also satisfies Eq. (1.1). We now prove that all λ_ν for $\nu \geq 1$ in (6.2) have positive real parts: $\text{Re} \lambda_\nu > 0$. This includes the statement that the eigenvalue $\lambda_0 = 0$ is nondegenerate. Although the proof to be given will be based upon the results of the stability considerations of Sec. V, it is not a trivial consequence of the stability properties since these have been established in the physical region only. Hyver (1972) and Keizer (1972) have proved the above statement by application of matrix theory. Let us assume now that for any of the λ_ν 's for $\nu \geq 1$, say for λ_1 , we have $\text{Re} \lambda_1 \leq 0$. Let us then look at a particular solution obtained from (6.2) by setting $c_1 \neq 0$, $c_2 = c_3 = \dots = 0$ and taking the real part

$$p_i(t) = \bar{p}_i + \text{Re} \{ c_1 u_i^{(1)} Q_i^{(1)}(t) e^{-\lambda_1 t} \}. \quad (6.3)$$

Since the system (1.1) is linear and homogeneous, we may multiply the right-hand side of (6.3) by an arbitrary factor to obtain a solution in the form

$$\tilde{p}_i(t) = C^{-1} [\bar{p}_i + \text{Re} \{ c_1 u_i^{(1)} Q_i^{(1)}(t) e^{-\lambda_1 t} \}]. \quad (6.4)$$

By choosing

$$C = \sum_i p_i(0) = 1 + \sum_i \text{Re} \{ c_1 u_i^{(1)} Q_i^{(1)}(0) \}, \quad (6.5)$$

we have normalized the solution $\tilde{p}_i(t)$ such that

$$\sum_i \tilde{p}_i(t) = \sum_i \tilde{p}_i(0) = 1. \quad (6.6)$$

Finally, we can always bring the

$$\tilde{p}_i(0) = C^{-1} [\bar{p}_i + \text{Re} \{ c_1 u_i^{(1)} Q_i^{(1)}(0) \}] \quad (6.7)$$

to satisfy

$$0 < \tilde{p}_i(0) < 1 \quad (6.8)$$

by choosing c_1 sufficiently small, since for the Kirchhoff steady state \bar{p}_i we have $0 < \bar{p}_i < 1$. Now the solution $\tilde{p}_i(t)$ satisfies all conditions of the stability theorem of Sec. V. This immediately implies either $\text{Re} \lambda_1 > 0$ or $Q_i^{(1)}(t) = \text{const}$

if $\text{Re}\lambda_1 = 0$. The latter possibility, however, is excluded since then $\bar{p}_i(t) = \text{const}$ would represent a steady state in the physical region different from the Kirchhoff steady state. This cannot be the case since the Kirchhoff steady state is unique in the physical region as mentioned at the end of Sec. V.

Summarizing our conclusions from Secs. III, IV, V and the present one we may now say that

(a) $-W_{ij}$ has exactly one nondegenerate eigenvalue $\lambda_0 = 0$ or, with other words,

$$r\{W_{ij}\} = N - 1 \quad (6.9)$$

which completes the inequality (3.5),

(b) all other eigenvalues of $-W_{ij}$ have positive real parts,

(c) the Kirchhoff steady state \bar{p}_i is unique in the full mathematical space of the normalized variables p_i , i.e., $\sum_i p_i = 1$, and every solution starting at arbitrary points in this space is asymptotically stable with respect to the \bar{p}_i .

VII. ENTROPY PRODUCTION AND THE GLANSDORFF-PRIGOGINE CRITERION OF STABILITY

As pointed out in the introductory Sec. I, we call a description of the nonequilibrium system S in terms of probability distributions $\{p_i\}$ over states $i = 1, 2, \dots, N$ a microscopic description even if the states i do not represent a complete quantum-mechanical or classical set of variables. In the two examples of Sec. II, the states i had been chosen as configurational states of a membrane pore or as states with given numbers of a molecule of type X , respectively, and thus are evidently not complete in the above sense. Nevertheless, the notation "microscopic" for such a description may be justified. This will become clear if we now turn to what we shall call a macroscopic or phenomenological thermodynamic description of the nonequilibrium system S .

From a thermodynamic point of view, the nonequilibrium system S is envisaged as a black box exposed to a well-defined set of generalized external thermodynamic forces due to the simultaneous coupling to different reservoir systems. The response of the system to this set of forces manifests itself in a corresponding set of generalized thermodynamic fluxes. For the membrane example in Sec. II, the force is proportional to the difference of the electrochemical potential of the ion across the membrane, and the flux is the number of ions penetrating across the membrane per time and area; for the reaction system in part (B) of Sec. II, force and flux are given as the overall affinity of the net reaction $A + B \rightleftharpoons C$ divided by the temperature T , and as the reaction rate as number of moles per time. We could equally well expose the system to fixed and given values of fluxes and observe the corresponding forces as its response, but since this alteration would not principally change the subsequent considerations, we usually refer to the former situation in order not to make the formulation too difficult.

The first step on our way from a microscopic to a macroscopic description of the nonequilibrium system S is to establish an expression P for what will turn out to be the entropy production of S . The way we shall derive

this expression P will seem a little artificial, however, it will be an essential aim of the following sections to prove that P obtained thereby satisfies all requirements to be imposed on the entropy production.

Once again our starting point is the assumption that the master equation (1.1) gives the microscopic dynamical evolution of the system S as far as we are interested in its internal degrees of freedom. From this master equation we now construct a fictitious system S' by the following prescriptions:

(a) S' is a materially open homogeneous system containing the chemical species X_1, X_2, \dots, X_N ;

(b) there are chemical reactions possible between pairs (X_i, X_j) of the components, $X_i \rightleftharpoons X_j$, such that the reaction rates are given as

$$J'_{ij} = \langle i | j \rangle c_j - \langle j | i \rangle c_i, \quad (7.1)$$

where c_i, c_j are the concentrations of X_i, X_j , respectively, and $\langle i | j \rangle, \langle j | i \rangle$ are the transition probabilities to be taken from the master equation (1.1);

(c) there may be further chemical components involved in the reaction between X_i and X_j not belonging to the set X_1, X_2, \dots, X_N ; such components are assumed to be fed into the system at constant concentrations and the values of their concentrations are incorporated into the constants $\langle i | j \rangle$ and $\langle j | i \rangle$.

It is clear that these prescriptions do not define S' in a unique way. Every system S' which satisfies the above prescriptions may be accepted as representative.

Due to (7.1) the time change of the concentration c_i of the component X_i in S' is given as

$$\frac{dc_i}{dt} = \sum_j J'_{ij}. \quad (7.2)$$

By choosing

$$p_i = c_i / \left(\sum_j c_j \right), \quad (7.3)$$

$[\sum_j c_j = \text{const, cf. (4.2)}]$ Eq. (7.2) becomes formally equivalent to the master equation (1.1). We therefore rewrite (7.1) as

$$J_{ij} = \langle i | j \rangle p_j - \langle j | i \rangle p_i \quad (7.4)$$

such that the reaction rates $J'_{ij} \sim J_{ij}$ with a proportionality factor independent of i, j .

Here J_{ij} as given by (7.1) is the generalized thermodynamic flux of the reaction $X_i \rightleftharpoons X_j$. The conjugated generalized thermodynamic force is the affinity defined as

$$A_{ij} = \log \langle i | j \rangle p_j / \langle j | i \rangle p_i \quad (7.5)$$

for an ideal system S' . Our definition (7.5) deviates from the usual definition of the affinity which contains an additional factor $k_B T$ in front of the log term, k_B being the Boltzmann constant, and T the temperature at which the reaction occurs. With this latter convention, however, the generalized force is then given by the affinity divided by the temperature so that eventually the temperature is canceled, in agreement with our definition (7.5) (apart from the factor k_B). Since the system S' is a fictitious one and was assumed to be homogeneous, the choice of a temperature would be completely irrelevant and there-

fore it is logical to start from the definition (7.5).

Having now defined generalized fluxes and forces in the system S' by (7.1) and (7.5) we are led to interpret the bilinear expression

$$P = \frac{1}{2} \sum_{i,j} J_{ij} A_{ij} = \frac{1}{2} \sum_{i,j} (\langle i|j \rangle p_j - \langle j|i \rangle p_i) \log \frac{\langle i|j \rangle p_j}{\langle j|i \rangle p_i} \quad (7.6)$$

as the entropy production in S' . [Equation (7.6) differs from the usual definition of P by a factor k_B and another factor contained in (7.3) as we have replaced J'_{ij} by J_{ij} .] Since S' was assumed to be homogeneous, the chemical reactions $X_i \rightleftharpoons X_j$ are indeed the only irreversible processes in S' and there will be no further contribution to P .

The question to be raised at this point is whether the entropy production P of the fictitious system S' has anything to do with the entropy production of the real system S which in the language of phenomenological thermodynamics would have to be expressed as a bilinear form of the fluxes and forces of the real system S , instead of that of the fictitious system S' . This will be an essential aim of the following sections VIII–X. In the context of the present section, however, we can already give two hints which will lead us to identify P of (7.6) with the entropy production of S .

First, we observe that P of (7.6) can be split into two contributions

$$P = P_1 + P_2, \quad (7.7)$$

where

$$P_1 = \frac{1}{2} \sum_{i,j} J_{ij} \log \frac{p_j}{p_i}, \quad (7.8)$$

$$P_2 = \frac{1}{2} \sum_{i,j} J_{ij} \log \frac{\langle i|j \rangle}{\langle j|i \rangle}. \quad (7.9)$$

It is easily verified that P_1 can be expressed as

$$P_1 = dS/dt, \quad (7.10)$$

where

$$S = - \sum_i p_i \log p_i \quad (7.11)$$

To prove (7.10) we only have to make use of the master equation (1.1).

Let us discuss briefly the physical background of the splitting of the total entropy production P into the contributions P_1 and P_2 . From the fact that P_1 is given as the time derivative of the expression S defined in (7.11) which would have been chosen as the entropy of the system S under equilibrium conditions, we conclude that the contribution P_2 is due to the coupling of the system to an external set of thermodynamic forces which prevent the system from achieving an equilibrium state. It should be emphasized that neither P_1 nor P_2 are necessarily positive but only that $P = P_1 + P_2 \geq 0$ as immediately follows from (7.6).

If the external reservoir systems were to involve some further external dissipative process, the total entropy production P would have to include some further term

P_3 to account for the corresponding external production of entropy. In this case, only the sum $P_1 + P_2 + P_3$ would be positive but not necessarily each of the contributions P_1, P_2, P_3 and neither partial sums. Thus the entropy production P of (7.6) could be interpreted as the minimal entropy production which is realized for ideal reservoir systems.

The second hint identifying P of (7.6) with the entropy production of the real system S comes from the formulation of the stability criterion of Glansdorff and Prigogine (1971) for the fictitious system S' . According to this criterion, a steady state of a thermodynamic system is stable if the second-order variation $\delta^2 P$ of its entropy production around the steady state, the so-called excess entropy production, is positive. With J_{ij} and A_{ij} as the fluxes and forces of the fictitious system S' defined by (7.4) and (7.5) the Glansdorff–Prigogine criterion then reads

$$\delta^2 P = \frac{1}{2} \sum_{i,j} \delta J_{ij} \cdot \delta A_{ij} \geq 0, \quad (7.12)$$

where from (7.4) and (7.5) we have

$$\delta J_{ij} = \langle i|j \rangle \delta p_j - \langle j|i \rangle \delta p_i, \quad (7.13)$$

$$\delta A_{ij} = (\delta p_j / \bar{p}_j) - (\delta p_i / \bar{p}_i), \quad (7.14)$$

and

$$\delta p_i = p_i - \bar{p}_i \quad (7.15)$$

are the fluctuations around the steady state the stability of which is to be examined. Inserting (7.14) and the fluctuation version of the master equation

$$\frac{d}{dt} \delta p_i = \sum_j \delta J_{ij} \quad (7.16)$$

into (7.12) and making use of $\delta J_{ij} = -\delta J_{ji}$, we obtain

$$\begin{aligned} \delta^2 P &= \frac{1}{2} \sum_{i,j} \delta J_{ij} \left(\frac{\delta p_j}{\bar{p}_j} - \frac{\delta p_i}{\bar{p}_i} \right) \\ &= - \sum_i \frac{\delta p_i}{\bar{p}_i} \sum_j \delta J_{ij} = - \sum_i \frac{\delta p_i}{\bar{p}_i} \frac{d}{dt} \delta p_i \\ &= \frac{d}{dt} \left\{ - \frac{1}{2} \sum_i \frac{1}{\bar{p}_i} (\delta p_i)^2 \right\} \geq 0. \end{aligned} \quad (7.17)$$

The Glansdorff–Prigogine criterion now has the usual form of a Liapunov stability criterion with

$$\delta^2 L = - \frac{1}{2} \sum_i \frac{1}{\bar{p}_i} (\delta p_i)^2 \quad (7.18)$$

as the corresponding Liapunov function. The deciding point of our present consideration is the fact that $\delta^2 L$ of (7.18) is nothing else than the negative second-order variation of the K functional which is obtained from (5.9) as

$$\begin{aligned} \delta^2 K &= \delta^2 \left\{ \sum_i p_i \log \frac{p_i}{\bar{p}_i} \right\} \\ &= \left\{ \sum_i (\bar{p}_i + \delta p_i) \log \left(\frac{\delta p_i}{\bar{p}_i} \right) \right\}^{(2)} \\ &= \frac{1}{2} \sum_i \frac{1}{\bar{p}_i} (\delta p_i)^2. \end{aligned} \quad (7.19)$$

This means that the Glansdorff-Prigogine criterion for the fictitious system S' coincides with the differential version of the global Liapunov criterion for our real system S and can thus be considered as a consequence or special case of the global criterion.

The relationship between the Glansdorff-Prigogine criterion and the K functional has been pointed out the first time by Schlögl (1971). A general discussion of the Glansdorff-Prigogine criterion in the light of Liapunov's theory has been given by De Sobrino (1975). From this latter discussion it becomes clear that for general macroscopic systems of chemical reactions the Glansdorff-Prigogine criterion is only a sufficient criterion of stability. There are macroscopic systems which do not satisfy this criterion as for example the macroscopic version of the system defined in Eq. (2.2). For our master equation systems S and hence for the fictitious systems S' derived from S , however, we have shown in (7.17) and (7.18) that the Glansdorff-Prigogine criterion is always satisfied.

VIII. MACROSCOPIC THERMODYNAMIC FORMULATION: CYCLES AND AFFINITIES

The generalized thermodynamic forces to which the real nonequilibrium system S is exposed when coupled to different reservoir systems are incorporated in the transition probabilities $\langle i|j \rangle$ of the master equation (1.1). Let us elucidate the relation between the thermodynamic forces and the $\langle i|j \rangle$ in the case of the two examples given in Sec. II. For this purpose, we multiply the transition probabilities as given by (2.1) for the membrane pore model along the two possible directions of the basic cyclic graph of Fig. 1(b). Taking the ratio of the two products, we obtain

$$\frac{\langle N|N-1 \rangle \langle N-1|N-2 \rangle \cdots \langle 2|1 \rangle \langle 1|N \rangle}{\langle N|1 \rangle \langle 1|2 \rangle \cdots \langle N-2|N-1 \rangle \langle N-1|N \rangle} = \frac{c}{c'} \exp(2N\phi) \\ = \exp\left(\frac{\Delta\eta}{k_B T}\right), \quad (8.1)$$

where

$$\Delta\eta = k_B T \log \frac{c}{c'} + zeF\Delta \quad (8.2)$$

is the over-all difference of the electrochemical potential of the involved ion across the membrane. Quite analogously, the ratio of the transition probability products along the two possible directions of a single cycle between the states $X-1$ and X in the second example of Sec. II (cf. Fig. 2) is obtained from (2.5) as

$$\frac{\langle X|X-1 \rangle^{(1)} \langle X-1|X \rangle^{(2)}}{\langle X|X-1 \rangle^{(2)} \langle X-1|X \rangle^{(1)}} = \frac{k_1 k_2 ab}{k'_1 k'_2 c} = \exp\left(\frac{\tilde{A}}{k_B T}\right), \quad (8.3)$$

where

$$\tilde{A} = k_B T \log \frac{k_1 k_2 ab}{k'_1 k'_2 c} \quad (8.4)$$

is the overall affinity of the reaction $A+B \rightleftharpoons C$. Note that the result \tilde{A} of (8.4) does not depend on the position of the cycle, i.e., on the states X and $X-1$ between which the cycle is situated. Both examples are homogeneous with respect to the temperature such that there is no am-

biguity with the factor T in (8.2) and (8.4).

Generalizing the above conclusions from our two examples, we assume for arbitrary systems governed by a master equation (1.1), the corresponding macroscopic forces to be determined by the cycles of the basic graph G in the same way as in (8.1) and (8.3). This assumption can be confirmed for all the numerous models which have been constructed on the basis of a master equation for transport across membranes and other nonequilibrium phenomena [cf., Hill, Kedem (1966)].

The aim of this section and of the next is to justify the above conjecture of associating the thermodynamic forces with the cycles of the graph G . To this end, we shall prove that the steady state value of the entropy production as given by (7.6) can be written as a bilinear expression

$$\bar{P} = \sum_{\alpha=1}^{\nu} A(\vec{C}_{\alpha}) F(\vec{C}_{\alpha}) \quad (8.5)$$

or forces $A(\vec{C}_{\alpha})$ and fluxes $F(\vec{C}_{\alpha})$ such that under steady state conditions

(a) $A(\vec{C}_{\alpha})$ and $F(\vec{C}_{\alpha})$ are uniquely determined by a fundamental set of cycles \vec{C}_{α} of the basic graph G ,

(b) the $A(\vec{C}_{\alpha})$ are independent of the steady state probabilities \bar{p}_i and thus only depend on the external coupling conditions as in (8.2) and (8.4),

(c) $A(\vec{C}_{\alpha}) = 0$ for all α is equivalent to $\bar{F}(\vec{C}_{\alpha}) = 0$ for all α which in turn is equivalent to $\langle i|j \rangle \bar{p}_j = \langle j|i \rangle \bar{p}_i$ for all independent transitions between the state i and j which means the thermodynamic equilibrium,

(d) if the steady state \bar{p}_i is a thermodynamic equilibrium, there is a linear relation between the $A(\vec{C}_{\alpha})$ and $F(\vec{C}_{\alpha})$ in the vicinity of the equilibrium,

$$A(\vec{C}_{\alpha}) = \sum_{\beta} L_{\alpha\beta} F(\vec{C}_{\beta}) \quad (8.6)$$

with

$$L_{\alpha\beta} = L_{\beta\alpha}.$$

Clearly, these findings would link the microscopic dynamic description of the system in the master equation (1.1) with the macroscopic thermodynamic description in terms of generalized thermodynamic forces and fluxes. Moreover, they justify the identification of the steady state value of P in (7.6) with the macroscopic entropy production of the real system S .

This raises two questions: how many cycles can be identified in a graph G and whether or not each of these corresponds to an independent thermodynamic force. To answer these questions, we have to go a little further into some elementary methods and theorems of the mathematical theory of graphs. In Sec. III, we have already introduced maximal trees $T(G)$ of G as connected, covering and circuit-free subgraphs of G . The edges of G which do not belong to $T(G)$ are called the chords of $T(G)$. The number of chords is given by $\nu = E - N + 1$, where E and N are the numbers of edges and vertices in G , respectively. $T(G)$ has the important property that if one of the chords s_1, \dots, s_{ν} is added to $T(G)$ the resulting subgraph $T(G) + s_{\alpha}$ contains exactly one circuit, say C_{α} , which is obtained from $T(G) + s_{\alpha}$ by removing all edges

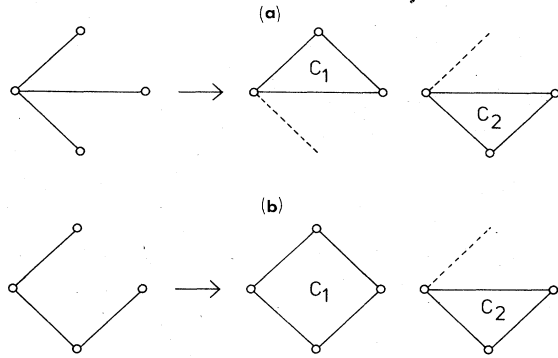


FIG. 5. Two possibilities to construct fundamental sets of circuits for the example given in Fig. 3; in parts (a) and (b) one starts from two different maximal trees of part (b) of Fig. 3. The circuit C_1 in (b) is the result of the \oplus -relation of C_1 and C_2 in (a).

which are not part of the circuit. The set of circuits $\{C_1, \dots, C_\nu\}$ obtained in this way is called a fundamental set. Fig. 5 shows the construction of a fundamental set for the example given in Fig. 3.

A well-known theorem of graph theory now proves that any circuit C of G can be represented as linear combination

$$C = \rho_1 C_1 \oplus \rho_2 C_2 \oplus \dots \oplus \rho_\nu C_\nu \quad (8.7)$$

of the circuits of a fundamental set where $\rho_\alpha = 1$ or 0 depending on whether the chord s_α belongs to C or not. The relation

$$C = C_1 \oplus C_2 \quad (8.8)$$

between two circuits C_1, C_2 is defined as to yield a subgraph C of G such that the set $E(C)$ of edges of C is the symmetric difference between the sets $E(C_1), E(C_2)$ of edges of C_1, C_2

$$E(C) = [E(C_1) - E(C_2)] \cup [E(C_2) - E(C_1)] \quad (8.9)$$

Eq. (8.9) means that C contains all edges of C_1 and C_2 which do not simultaneously belong to C_1 and C_2 . Figure 6 gives two examples for the relation (8.8).

It should be noted, that the result C of Eq. (8.8) need not be a simple circuit, but is perhaps a superposition

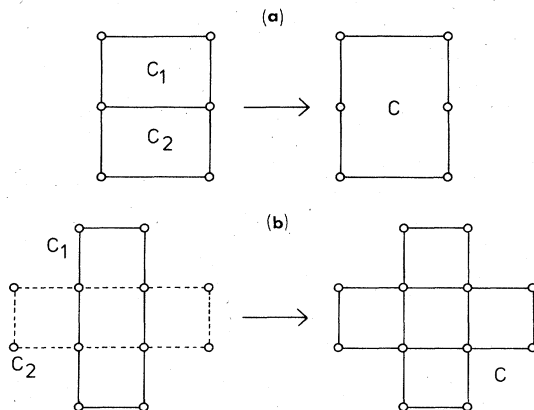


FIG. 6. Two examples for the relation $C_1 \oplus C_2 = C$, the result being a simple circuit in (a) and a quasicircuit in (b).

of circuits [case (b) in Fig. 5], a so-called quasicircuit, i.e., a subgraph in which every vertex is connected with an even number of neighboring vertices.

For a unique definition of the thermodynamic force A of a circuit like that in (8.1) or (8.3) we not only need the topological structure of C in G but also a reference orientation of C since A changes its sign when C changes its orientation. For this purpose, we first choose an arbitrary reference orientation for each edge x_e of G ($1 \leq e \leq E$, E being the number of edges in G) by defining a matrix

$$D(i, x_e) = \begin{cases} +1 & \text{if } i \leftarrow x_e \\ -1 & \text{if } i \rightarrow x_e \\ 0 & \text{otherwise} \end{cases} \quad (8.10)$$

where $i \leftarrow x_e$ and $i \rightarrow x_e$ denote that the reference orientation of edge x_e is directed into the vertex i and out of vertex i , respectively. A particularly simple choice of reference directions for edges $x_e \hat{=} (j, k)$ would be $k \rightarrow j$ if and only if $j < k$ and vice versa. This special choice is expressed in terms of the above matrix D as $D[i, (j, k)] = +1$ if $i = j < k$ or $i = k < j$, $D[i, (j, k)] = -1$ if $i = j > k$ or $i = k > j$, and $D[i, (j, k)] = 0$ otherwise.

Letting (x_1, \dots, x_E) be an arbitrary ordering of the edges of G such that the first ν of them coincide with the chords (s_1, \dots, s_ν) of a fundamental set, any directed subgraph \vec{P} of G , i.e., a subgraph \vec{P} of G with arbitrary directions on its edges, is uniquely characterized by numbers $S_e(\vec{P})$ with

$$S_e(\vec{P}) = \begin{cases} +1 & \text{if } \vec{P}, x_e \text{ parallel,} \\ -1 & \text{if } \vec{P}, x_e \text{ antiparallel,} \\ 0 & \text{if } x_e \text{ not in } \vec{P}, \end{cases} \quad (8.11)$$

where \vec{P}, x_e parallel means that \vec{P} contains edge x_e in its reference orientation, and \vec{P}, x_e antiparallel analogously.

Allowing $S_e(\vec{P})$ to adopt any positive or negative integer or zero we generalize the concept of a subgraph in that \vec{P} may then contain an edge of G several times. The generalized subgraphs form a linear vector space if we define

$$S_e(c_1 \vec{P}_1 + c_2 \vec{P}_2) = c_1 S_e(\vec{P}_1) + c_2 S_e(\vec{P}_2) \quad (8.12)$$

c_1, c_2 being integers.

Eventually, we introduce a linear operator ∂_i acting on directed subgraphs as

$$\partial_i \vec{P} = \sum_{e=1}^E D(i, x_e) S_e(\vec{P}) \quad (8.13)$$

Calling the oriented or directed versions of circuits and quasicircuits cycles and quacycles, respectively, we immediately see that

$$\partial_i \vec{Q} = 0 \quad (8.14)$$

may be considered as the defining equation for quacycles. [Eq. (8.14) is often referred to as Tellegen's theorem].

We can now solve our original problem. Let \vec{C} be any cycle of G and let the corresponding (undirected) circuit have the representation (8.7) with respect to an arbitrary fundamental set of circuits. From the latter we construct a fundamental set of cycles by assigning arbi-

trary orientations to the C_1, \dots, C_ν to obtain $\vec{C}_1, \dots, \vec{C}_\nu$. Defining a scalar product

$$(\vec{C}, \vec{C}_\alpha) = S_\alpha(\vec{C}) S_\alpha(\vec{C}_\alpha) \quad 1 \leq \alpha \leq \nu \quad (8.15)$$

which may be any positive or negative integer or zero, we consider the subgraph

$$\vec{Q} = \sum_{\alpha=1}^{\nu} (\vec{C}, \vec{C}_\alpha) \vec{C}_\alpha. \quad (8.16)$$

Since the \vec{C}_α are cycles,

$$\partial_i \vec{C}_\alpha = 0 \quad (8.17)$$

and ∂_i is linear, we conclude

$$\partial_i \vec{Q} = 0 \quad (8.18)$$

such that \vec{Q} of (8.16) is a quasicycle. Furthermore, it is evident from (8.15) that the corresponding quasicircuit Q contains the same chords as the circuit C . Since the chords of a fundamental set uniquely characterize a quasicircuit, we conclude $Q = C$ which says that Q is a circuit. Finally, \vec{Q} and \vec{C} are parallel on all chords s_α with $(\vec{C}, \vec{C}_\alpha) \neq 0$ such that $\vec{Q} = \vec{C}$ and

$$\vec{C} = \sum_{\alpha=1}^{\nu} (\vec{C}, \vec{C}_\alpha) \vec{C}_\alpha. \quad (8.19)$$

Comparing (8.7) and (8.19) we also have

$$\rho_\alpha = |(\vec{C}, \vec{C}_\alpha)|. \quad (8.20)$$

The significance of (8.19) lies in the fact that orientation can be included in the concept of the linear vector space of the circuits such that the oriented edges of G which occur on the right-hand side of Eq. (8.19), but not in \vec{C} cancel each other completely.

The representation (8.19) of a cycle \vec{C} of the graph G by a fundamental set of cycles is illustrated in Fig. 7.

The arrows along the edges of the graph in Fig. 7 indicate the reference orientations of the edges. The fundamental set of cycles $\vec{C}_1, \vec{C}_2, \vec{C}_3$ drawn into Fig. 7 is generated by a maximal tree with chords $s_1 = (1, 5)$, $s_2 = (3, 4)$, $s_3 = (4, 5)$. The $S_\alpha(\vec{C}_\alpha)$ of Eq. (8.11) are given as $+1, -1, -1$ for $\alpha = 1, 2, 3$ and $S_\alpha(\vec{C}_\beta) = 0$ if $\alpha \neq \beta$. Assuming that we want to represent the cycle $\vec{C} = (1, 2, 4, 5, 1)$ with reference orientation in this order of vertices, we simply have $S_\alpha(\vec{C}) = +1, 0, -1$ and thus by insertion into (8.15) and (8.19) $\vec{C} = \vec{C}_1 + \vec{C}_3$.

It is now obvious how the definitions (8.1) and (8.3) of the force $A(\vec{C})$ of an arbitrary cycle \vec{C} in G has to be generalized, namely

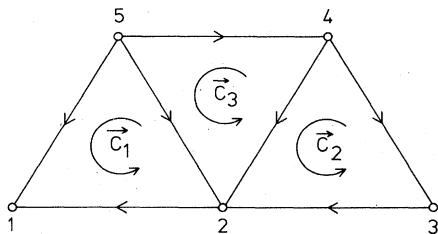


FIG. 7. Example to illustrate the operations defined in Sec. VIII for the inclusion of orientation of circuits and reference orientation of edges (A detailed description of the example is given in the text of Sec. VIII).

$$A(\vec{C}) = \sum_{e=1}^E S_e(\vec{C}) \log \frac{\langle i | j \rangle}{\langle j | i \rangle} \quad (8.21)$$

where it is understood on the right-hand side of (8.21) that the reference orientation of edge x_e is such that x_e is directed from j to i . It is consistent not to include a factor $k_B T$ into the definition (8.21) since $A(\vec{C})$ is meant as a thermodynamic force whereas the forces corresponding to the examples given in (8.2) and (8.4) are given as $\Delta\eta/T$ and \tilde{A}/T (for homogeneous temperatures).

It is easy to show that we could also have defined $A(\vec{C})$ as the sum of the affinities along the edges of \vec{C}

$$A(\vec{C}) = \sum_{e=1}^E S_e(\vec{C}) A_e \quad (8.22)$$

where according to (7.5) the affinity A_e of edge x_e is given by

$$A_e = \log \frac{\langle i | j \rangle p_j}{\langle j | i \rangle p_i}. \quad (8.23)$$

The right-hand sides of (8.21) and (8.22) are equal since

$$\sum_{e=1}^E S_e(\vec{C}) \log \frac{p_j}{p_i} = 0. \quad (8.24)$$

Note that although A_e depends on the microstate $\{p_i\}$ of the system, the affinity $A(\vec{C})$ along a cycle does not.

The essential result of this section is obtained by inserting the fundamental representation of cycle \vec{C} as given in Eq. (8.19) into (8.22). By making use of the linearity of $S_\alpha(\vec{C})$, cf. Eq. (8.12), we get

$$\begin{aligned} A(\vec{C}) &= \sum_{e=1}^E S_e \left(\sum_{\alpha=1}^{\nu} (\vec{C}, \vec{C}_\alpha) \vec{C}_\alpha \right) A_e, \\ &= \sum_{\alpha=1}^{\nu} (\vec{C}, \vec{C}_\alpha) \sum_{e=1}^E S_e(\vec{C}_\alpha) A_e, \\ &= \sum_{\alpha=1}^{\nu} (\vec{C}, \vec{C}_\alpha) A(\vec{C}_\alpha), \end{aligned} \quad (8.25)$$

where

$$A(\vec{C}_\alpha) = \sum_{e=1}^E S_e(\vec{C}_\alpha) A_e \quad (8.26)$$

is again independent of the microstate. Equation (8.25) confirms a basic assumption of the phenomenological theory of irreversible thermodynamics: an arbitrary macroscopic generalized force $A(\vec{C})$ associated with one of the cycles of the basic graphs is a linear combination of the forces $A(\vec{C}_\alpha)$ associated with a fundamental set of cycles, the coefficients being $+1, -1$ or 0 depending on whether \vec{C} is parallel or antiparallel to \vec{C}_α or does not contain \vec{C}_α . A fundamental set of (undirected) circuits is obtained by choosing an arbitrary maximal tree $T(G)$ in G , successively adding one of the chords to $T(G)$ and removing all edges which are not part of the generated circuit. From the fundamental set of circuits a fundamental set of cycles is obtained by giving arbitrary orientations to the circuits of the set. The dimension of the fundamental sets is $\nu = E - N + 1$.

The thermodynamic significance of cycles in the representative graph and the possibility of creating new cycles by linear combinations was first observed by Bak (1963). In Bak's theory, however, the cycles and their affinities only appear in Wegscheider's condition for the

eigenvalues λ , of Section V, to have positive real parts. In this condition, it is assumed that all affinities $A(\vec{C}_\alpha)$ vanish. Interpreting the $A(\vec{C}_\alpha)$ as the phenomenological forces, Wegscheider's condition reduces to the condition of thermal equilibrium (compare Section X). As we have shown in Section VI, the positivity of the real parts of the eigenvalues λ can be proved under much less restrictive conditions.

The fact that the cycles of G are related to the phenomenological forces, follows from Kirchhoff's theorem (compare Section III). For particular models, this relationship has been pointed out by Hill (1968).

IX. STEADY STATE: KIRCHHOFF'S CURRENT LAW AND MACROSCOPIC ENTROPY PRODUCTION

For any edge x_e with reference orientation from j to i in the basic graph G of our system we define in correspondence with Eq. (7.4) as steady state flux

$$\bar{J}_e = \bar{J}_{ij} = \langle i | \bar{p}_j \rangle - \langle j | \bar{p}_i \rangle. \quad (9.1)$$

The rate equation (1.1) of our system can simply be expressed in the steady state as

$$\sum_j \bar{J}_{ij} = 0 \quad (9.2)$$

By making use of definitions (7.6) and (8.1) we get from (9.2)

$$\sum_{e=1}^E D(i, x_e) \bar{J}_e = 0 \quad (9.3)$$

which is Kirchhoff's Current Law (KCL) for each vertex i . Note that KCL in the form of (9.3) is restricted to the steady state, but not necessarily to thermal equilibrium. We could easily generalize KCL to include even non-steady state situations by introducing capacitive elements for nonvanishing dp_i/dt but for our subsequent considerations there is no need for this generalization.

Let $T(G)$ be a maximal tree of G with chords (s_1, \dots, s_ν) and let $(\vec{C}_1, \dots, \vec{C}_\nu)$ be a fundamental set of cycles derived from $T(G)$. As the steady state flux $F(\vec{C}_\alpha)$ along the cycle \vec{C}_α of the fundamental set we define

$$F(\vec{C}_\alpha) = S_\alpha(\vec{C}_\alpha) \bar{J}_\alpha, \quad (9.4)$$

where \bar{J}_α is the steady state flux of the chord s_α of \vec{C}_α relative to $T(G)$. By repeatedly applying KCL to the steady state fluxes in G we easily obtain for the steady state flux \bar{J}_e along any of the edges x_e of G

$$\bar{J}_e = \sum_{\alpha=1}^{\nu} S_e(\vec{C}_\alpha) F(\vec{C}_\alpha). \quad (9.5)$$

If x_e happens to coincide with one of the chords s_α , Eq. (9.5) reduces to (9.4) since $S_\alpha^2(\vec{C}_\alpha) = 1$. If x_e in (9.5) is part of a bridge in G , i.e., if there exists no circuit in G which contains x_e , we derive from (9.5) $\bar{J}_e = 0$. Thus, if we restrict ourselves to the study of the steady state, we may remove all edges along bridges, so-called cut edges, from G and thereby decompose our system into unconnected sub-systems.

In Section VII, Eq. (7.6), we have written the entropy production P of the fictitious system S' for arbitrary microstates p_i as

$$P = \frac{1}{2} \sum_{i,j} J_{ij} A_{ij}. \quad (9.6)$$

Introducing $A_e \equiv A_{ij}$, $J_e \equiv J_{ij}$ into (9.6) where edge x_e has reference orientation from j to i , we can rewrite (9.6) as

$$P = \sum_{e=1}^E J_e A_e. \quad (9.7)$$

Let us now consider the entropy production \bar{P} in the steady state. By successively inserting Eq. (9.5) and Eq. (8.26) into (9.7) we derive

$$\begin{aligned} \bar{P} &= \sum_{e=1}^E \bar{J}_e A_e = \sum_{\alpha=1}^{\nu} F(\vec{C}_\alpha) \sum_{e=1}^E S_e(\vec{C}_\alpha) A_e \\ &= \sum_{\alpha=1}^{\nu} F(\vec{C}_\alpha) A(\vec{C}_\alpha). \end{aligned} \quad (9.8)$$

This result already confirms part of the program set up in Sec. VIII following Eq. (8.5): Eq. (9.8) proves Eq. (8.5), point (a) is expressed by (8.26) and the inverse of (9.5), which due to KCL is unique in the steady state, and point (b) is obtained by applying (8.21) to $\vec{C} = \vec{C}_\alpha$ for all cycles \vec{C}_α of the fundamental set.

X. THERMAL EQUILIBRIUM: KIRCHHOFF'S VOLTAGE LAW, THE PHENOMENOLOGICAL COEFFICIENTS AND ONSAGER'S RECIPROCITY RELATIONS

Thermal equilibrium is a particular steady state \bar{p}_i^0 which on the microscopic level may be defined by the condition of "complete" detailed balance, i.e., by postulating

$$\bar{J}_{ij}^0 = \langle i | \bar{p}_j^0 \rangle - \langle j | \bar{p}_i^0 \rangle = 0 \quad (10.1)$$

for all independent transitions between all pairs of states (i, j) . If there is no transition between a pair of states (i, j) , condition (10.1) is identically satisfied since in this case we have $\langle i | \bar{p}_j \rangle = \langle j | \bar{p}_i \rangle = 0$ independent of the values of \bar{p}_i .

It seems worth while to point out in this context that the equilibrium condition (10.1) applied to the reaction system of Sec. II(B) means

$$\bar{J}_{X, X-1}^{(\rho)0} = \langle X | X-1 \rangle^{(\rho)} \bar{p}^0(X-1) - \langle X-1 | X \rangle^{(\rho)} \bar{p}^0(X) = 0 \quad (10.2)$$

separately for $\rho=1$ and $\rho=2$. On the other hand, an arbitrary steady state of this system is defined as

$$\bar{J}_{X, X-1}^{(1)} + \bar{J}_{X, X-1}^{(2)} = 0. \quad (10.3)$$

The basic graph of this system is a double chain as shown in Fig. 2. The left-hand side of (10.3) is the total flux along this double chain. Then KCL, Eq. (9.3), implies that, first of all, the total flux on the left-hand side of (10.3) is constant, i.e., independent of X . Since the double chain ends at least at $X=0$, the constant total flux vanishes.

Clearly, (10.2) satisfies (10.3) but not necessarily vice versa. Indeed, if there is a finite overall affinity \bar{A} as defined by (8.4) there will also be a finite flux $\bar{J}_{X, X-1}^{(1)} = -\bar{J}_{X, X-1}^{(2)} = \bar{J}_{X-1, X}^{(2)}$ along all cycles of the double chain. This is easily seen by evaluating the steady state condition (10.3) as

$$\bar{p}(X-1) = \frac{\langle X-1|X \rangle^{(1)} + \langle X-1|X \rangle^{(2)}}{\langle X|X-1 \rangle^{(1)} + \langle X|X-1 \rangle^{(2)}} \bar{p}(X) \quad (10.4)$$

which upon insertion into $\bar{J}_{X,X-1}^{(e)}$ leads to

$$\begin{aligned} \bar{J}_{X,X-1}^{(1)} &= -\bar{J}_{X,X-1}^{(2)} \\ &= \left\{ \exp\left(\frac{\tilde{A}}{k_B T}\right) - 1 \right\} \frac{\langle X|X-1 \rangle^{(2)} \langle X-1|X \rangle^{(1)}}{\langle X|X-1 \rangle^{(1)} + \langle X|X-1 \rangle^{(2)}} \cdot \bar{p}(X) \neq 0 \\ &\quad \text{if } \tilde{A} \neq 0 \end{aligned} \quad (10.5)$$

Further equivalent definitions of equilibrium in the rate equations are discussed by Thomsen (1953). In the macroscopic theory of irreversible thermodynamics, thermal equilibrium is defined by

$$F_\alpha = 0 \quad (10.6)$$

for all macroscopic fluxes F_α , or equivalently by

$$A_\alpha = 0 \quad (10.7)$$

for all macroscopic forces A_α .

Identifying the F_α of (10.6) with the fluxes $F(\vec{C}_\alpha)$ along the cycles as defined in (9.4), we easily see that the microscopic and macroscopic versions, (10.1) and (10.6) respectively, of defining the thermal equilibrium are equivalent. Indeed, if (10.1) holds for all edges, it also holds for the chords s_α of the cycles \vec{C}_α , and thus we have from (9.4) $F(\vec{C}_\alpha) = 0$ for all cycles \vec{C}_α . On the other hand, if $F(\vec{C}_\alpha) = 0$ for all \vec{C}_α , we derive from (9.5) $\bar{J}_e^0 = 0$ for all edges x_e of G .

What remains to be proved, is the equivalence between (10.6) and (10.7) if the A_α of (10.7) are identified with the $A(\vec{C}_\alpha)$ of (8.26). Let us start by assuming that $F(\vec{C}_\alpha) = 0$ for all cycles \vec{C}_α . As shown above, this implies $\bar{J}_e^0 = 0$ for all edges x_e or

$$\bar{J}_e^0 = \bar{J}_{ij}^0 = \langle i|j \rangle \bar{p}_j^0 - \langle j|i \rangle \bar{p}_i^0 = 0 \quad (10.8)$$

if edge x_e has reference orientation from j to i . Since $\langle j|i \rangle \neq 0$ if x_e exists and $p_i > 0$ (cf. Sec. IV), we obtain from Eq. (10.8)

$$\langle i|j \rangle \bar{p}_j^0 / \langle j|i \rangle \bar{p}_i^0 = 1, \quad (10.9)$$

and thus from (7.5)

$$\bar{A}_e^0 = \bar{A}_{ij}^0 = \log \frac{\langle i|j \rangle \bar{p}_j^0}{\langle j|i \rangle \bar{p}_i^0} = 0 \quad (10.10)$$

for all edges x_e . Inserting (10.10) into (8.26) we conclude $A(\vec{C}_\alpha) = 0$ for all cycles \vec{C}_α .

To prove the second part of the equivalence, let us assume that at least one of the $F(\vec{C}_\alpha)$ is nonzero. As a consequence, there must be at least one edge in G , say x_1 , along which the steady state flux does not vanish, for example along the chord s_α of \vec{C}_α . Moreover, KCL then implies the existence of a cycle \vec{C} with edges (x_1, \dots, x_λ) , $\lambda \leq E$, such that

$$S_e(\vec{C}) \bar{J}_e > 0 \quad e = 1, \dots, \lambda \quad (10.11)$$

Let the reference orientations of x_1, \dots, x_λ be such that $S_e(\vec{C}) = +1$ for $e = 1, \dots, \lambda$. The force along \vec{C} is then given by

$$A(\vec{C}) = \sum_{e=1}^{\lambda} A_e = \sum_{e=1}^{\lambda} \log \frac{\langle i|j \rangle \bar{p}_j}{\langle j|i \rangle \bar{p}_i}, \quad (10.12)$$

where again x_e has reference orientation from j to i . From (10.11), $\bar{J}_e > 0$, we derive

$$\langle i|j \rangle \bar{p}_j / \langle j|i \rangle \bar{p}_i > 1 \quad (10.13)$$

and hence $A(\vec{C}) > 0$. Due to (8.19), \vec{C} can be represented by a linear combination of the cycles \vec{C}_α of the fundamental set, the coefficients being identical with that in Eq. (8.25), where $A(\vec{C})$ is given as a linear combination of the $A(\vec{C}_\alpha)$. Thus, not all of the $A(\vec{C}_\alpha)$ can vanish if $A(\vec{C}) > 0$, q.e.d.

Let us emphasize the fact that the equivalence proofs just given depend on the steady state condition. Clearly, the fluxes along single edges of G can be finite during fluctuations of the system even if all forces $A(\vec{C}_\alpha)$ vanish. The equivalence of (10.1), (10.6), and (10.7) in the steady state proves point (c) of the program which we have established in the context of Eq. (8.5).

Condition (10.7) for thermal equilibrium is identical with Kirchhoff's voltage Law (KVL). It is easy to show that for purely electric systems the affinities reduce to voltage differences. In our version of representing systems described by a master equation like that in (1.1) by graphs or networks, KVL is thus restricted to thermal equilibrium, whereas KCL was restricted to the steady state. It should be noted once again that the question whether KCL and KVL are satisfied or not for restricted or unrestricted states of the system, depends definitely on the network language which is used to represent the system. Oster, Desoer, Perelson and Katchalsky (1971, 1973) have developed a different way of representing even nonlinear equations of systems by so-called bond-graph networks. In the language of bond graphs, KCL and KVL are satisfied for arbitrary states of the system.

Let us complete our discussion of the thermal equilibrium by establishing the linear relations between the phenomenological fluxes and forces near the equilibrium as stated as point (d) of our program following Eq. (8.5). This derivation becomes a very simple procedure on the basis of our formalism. For this purpose, we consider steady states \bar{p}_i of our system near the equilibrium state \bar{p}_i^0 such that

$$z_i = \frac{\bar{p}_i - \bar{p}_i^0}{\bar{p}_i^0} \ll 1. \quad (10.14)$$

The affinity \bar{A}_e of an edge x_e with reference orientation from j to i in the state \bar{p}_i is given by

$$\begin{aligned} \bar{A}_e &= \log \frac{\langle i|j \rangle \bar{p}_j}{\langle j|i \rangle \bar{p}_i} \\ &= \log \frac{\langle i|j \rangle \bar{p}_j^0}{\langle j|i \rangle \bar{p}_i^0} + \log \frac{1+z_j}{1-z_i} \end{aligned} \quad (10.15)$$

Due to (10.9) or (10.10), the first contribution on the right-hand side of (10.15) vanishes. In the second contribution, we expand in powers of z_i, z_j up to first-order terms to obtain

$$\begin{aligned} \bar{A}_e &= z_j - z_i = (\langle i|j \rangle \bar{p}_j - \langle j|i \rangle \bar{p}_i) / q_e \\ &= \bar{J}_e / q_e, \end{aligned} \quad (10.16)$$

where

$$q_e = \langle i|j \rangle \bar{p}_j^0 = \langle j|i \rangle \bar{p}_i^0, \quad (10.17)$$

and again use has been made of Eq. (10.9). Inserting (10.16) into (8.26) and expressing \vec{J}_e by Eq. (9.5) we obtain for the cyclic force $A(\vec{C}_\alpha)$

$$\begin{aligned} A(\vec{C}_\alpha) &= \sum_{e=1}^E S_e(\vec{C}_\alpha) \bar{A}_e \\ &= \sum_{e=1}^E \frac{1}{q_e} S_e(\vec{C}_\alpha) \vec{J}_e, \\ &= \sum_{\beta=1}^V \sum_{e=1}^E \frac{1}{q_e} S_e(\vec{C}_\alpha) S_e(\vec{C}_\beta) \cdot F(\vec{C}_\beta), \\ &= \sum_{\beta=1}^V L_{\alpha\beta} F(\vec{C}_\beta), \end{aligned} \quad (10.18)$$

where

$$L_{\alpha\beta} = \sum_{e=1}^E \frac{1}{q_e} S_e(\vec{C}_\alpha) S_e(\vec{C}_\beta). \quad (10.19)$$

Without any further calculations we immediately derive from Eq. (10.19) that the phenomenological coefficients $L_{\alpha\beta}$ fulfill Onsager's reciprocity relations

$$L_{\alpha\beta} = L_{\beta\alpha} \quad (10.20)$$

One could even argue that the expression (10.19) bears some formal similarity to the Kubo representation of linear phenomenological coefficients, but we will not overstress this relationship. From a network point of view, (10.20) expresses the reciprocity property of our graphs or networks which, however, in our case is restricted to the vicinity of the thermodynamic equilibrium. For arbitrary nonequilibrium situations in our graphs or networks, the reciprocity property is in general not valid, the reason being that the transitions between states i and j are so-called 2-pole elements or, in the language of electric circuit theory, 4-pole elements which are generally not reciprocal. In any case, (10.18) and (10.20) prove point d and hence complete the full program established in Sec. VIII.

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