

## **Fluxes and the Elimination of Fast-Relaxing Variables**

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The behavior of fluxes under elimination of fast-relaxing variables from linear dynamical evolution equations is investigated. It is found that the fluxes corresponding to evolution equations which result from eliminations do not in general yield an adequate representation of the fluxes corresponding to the evolution equations from which the variables have been eliminated. In all examples considered, a discrepancy occurs when the eliminations reduce a cycle with nonzero thermodynamic force to a single state. The entropy production corresponding to the evolution equations resulting from the eliminations lacks terms corresponding to such cycles.

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**KEY WORDS:** Fast-relaxing variables; adiabatic elimination; master equation; first-order kinetics; fluxes; entropy production.

### **1. INTRODUCTION**

The equations describing the dynamical evolution of the population properties of a system often allow for a classification of the population variables on the basis of the orders of magnitude of their relaxation times. If two or more time scales are well separated, the dynamical evolution of the population properties may be adequately described for long times by a simpler set of equations obtained by elimination of the faster-relaxing variables. Such eliminations (explicit and implicit) are common procedures in many fields, especially in chemical kinetics,<sup>(1)</sup> where one may refer to transient intermediates and fast equilibria.<sup>(2)</sup> They have also been an aid in developing laser theory.<sup>(3,4)</sup> A formal footing for the elimination techniques has been provided by Haken in the context of master equations<sup>(3)</sup> and Fokker-

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Planck equations.<sup>(3,5)</sup> In reference to the former, Schnakenberg<sup>(6)</sup> has pointed out that most master equations are the result of several implicit eliminations.

For many systems, the rates of processes occurring in the system are of as great interest as the population properties, or perhaps even of greater interest. This is especially the case for systems with nonequilibrium stationary states. The rates are normally given as fluxes defined in terms of the variables and parameters of the dynamical evolution equations for the population properties. Thus, in the case of the elimination of fast-relaxing variables there will be a set of fluxes  $J$  corresponding to the original dynamical evolution equations, and another set of fluxes  $Y$  corresponding to the dynamical evolution equations obtained from the original ones by the elimination of fast-relaxing variables. As noted above, the elimination leaves the population properties adequately described by the resulting evolution equations for long times. However, since this is the criterion for the validity of the elimination, it is not clear that the fluxes, originally given as the  $J$ 's, are still adequately represented by the  $Y$ 's (for long times, of course).

In more formal terms, we have an original set of dynamical evolution equations in terms of the population variables  $p_i$  with corresponding fluxes  $J(p_i)$ . Upon the elimination of fast-relaxing variables, we obtain a new set of evolution equations in terms of new population variables  $q_k$  with corresponding fluxes  $Y(q_k)$ . Now the transformation  $p_i \rightarrow q_k$  allows us to write the  $J$ 's as functions of the  $q_k$ . The question being asked here then becomes: may the  $J(q_k)$  be adequately represented by the  $Y(q_k)$  for long times?

The purpose of this paper is to show that the answer to this question is, in general, no. This will be accomplished by way of a few simple examples involving linear dynamical evolution equations (master or first-order kinetic equations). It will be argued that the answer "no" arises only for systems with nonequilibrium stationary states when the elimination of fast-relaxing variables also eliminates a cycle with nonzero thermodynamic force from the system's kinetic diagram.<sup>(2)</sup> It follows, then, that the entropy production of the Glansdorff-Prigogine stability criterion for the dynamical evolution equations resulting from the elimination of fast-relaxing variables will be lacking term(s) corresponding to the eliminated cycle(s).

## 2. THE BASIC EQUATIONS

We consider dynamical evolution equations of the form

$$\dot{p}_i = \frac{d}{dt} p_i = - \sum_{\substack{j=1 \\ j \neq i}}^N (a_{ij} p_i - a_{ji} p_j), \quad \sum_{i=1}^N p_i = 1 \quad (1)$$

where  $p_i$  is the probability that the system is in state  $i$  of  $N$  possible states, and  $a_{ij}$  is the transition probability per unit time from state  $i$  to state  $j$ . To allow for transitions between states  $i$  and  $j$  via different pathways,<sup>(2,6)</sup> we write

$$a_{ij} = \sum_{\alpha=1}^{n_{ij}} a_{ij}(\alpha), \quad n_{ij} = n_{ji} \tag{2}$$

where  $a_{ij}(\alpha)$  is the transition probability per unit time from state  $i$  to state  $j$  via pathway  $\alpha$ . The generalization in Eq. (2) is necessary for a proper definition of the transition fluxes:

$$J_{ij}(\alpha) = -J_{ji}(\alpha) = a_{ij}(\alpha)p_i - a_{ji}(\alpha)p_j \tag{3}$$

which is the net rate of transition from state  $i$  to state  $j$  via pathway  $\alpha$ . A particularly clear example with multiple pathways may be found in Ref. 6. One may also be convinced of the necessity of Eq. (2) by noting that detailed balance at equilibrium requires that all  $J_{ij}(\alpha) = 0$ .<sup>(2,6)</sup>

Upon the elimination of fast-relaxing variables from Eq. (1), the new evolution equations become

$$\dot{q}_k = - \sum_{\substack{l=1 \\ l \neq k}}^M (b_{kl}q_k - b_{lk}q_l), \quad \sum_{k=1}^M q_k = 1, \quad M \leq N \tag{4}$$

with

$$b_{kl} = \sum_{\beta=1}^{m_{kl}} b_{kl}(\beta), \quad m_{kl} = m_{lk} \tag{5}$$

and corresponding transition fluxes

$$Y_{kl}(\beta) = -Y_{lk}(\beta) = b_{kl}(\beta)q_k - b_{lk}(\beta)q_l \tag{6}$$

The  $q$ 's and  $b$ 's are again to be interpreted as probabilities and transition probabilities, respectively; however, note that  $q_i$  is not necessarily equal to  $p_i$ , since the states involved in Eqs. (4)–(6) are not in general identical with those in Eqs. (1)–(3).

### 3. EXAMPLES

We now proceed to give three simple examples where, after the elimination of fast-relaxing variables from Eq. (1), the  $J_{ij}(\alpha)$  [Eq. (3)] may not all be expressed in terms of the  $Y_{kl}(\beta)$  [Eq. (6)].

#### 3.1.

As a first example, let us consider the case where all  $n_{ij} = 1$  in Eq. (2) and the transition probabilities  $a_{N,N-1}$ ,  $a_{N-1,N}$ ,  $a_{N-1,N-2}$ ,  $a_{N-2,N-1}$  are

several orders of magnitude larger than the other  $a_{ij}$  of Eqs. (1)–(3). [We have dropped the index  $\alpha$  from  $a_{ij}(\alpha)$  since it is always 1.] For long times, the following relations hold approximately<sup>(2,3)</sup>:

$$a_{N,N-1}p_N = a_{N-1,N}p_{N-1}, \quad a_{N-1,N-2}p_{N-1} = a_{N-2,N-1}p_{N-2} \quad (7)$$

Upon defining a new probability

$$q_M = p_{N-2} + p_{N-1} + p_N \quad (8)$$

$p_{N-2}$ ,  $p_{N-1}$ , and  $p_N$  may be expressed in terms of  $q_M$ ; substitution of these results into Eq. (1) yields Eq. (4), where

$$M = N - 2, \quad q_k = p_k, \quad k \leq M - 1$$

$$m_{kl} = \begin{cases} 1, & k \leq M - 1, & l \leq M - 1 \\ 3, & k \leq M - 1, & l = M \\ 3, & k = M, & l \leq M - 1 \end{cases}$$

$$b_{kl}(1) = a_{kl}, \quad b_{lk}(1) = a_{lk}; \quad k \leq M - 1, \quad l \leq M - 1 \quad (9)$$

$$\left. \begin{aligned} b_{kM}(1) &= a_{k,N-2}, & b_{Mk}(1) &= a_{N,N-1}a_{N-1,N-2}a_{N-2,k}/s \\ b_{kM}(2) &= a_{k,N-1}, & b_{Mk}(2) &= a_{N-2,N-1}a_{N,N-1}a_{N-1,k}/s \\ b_{kM}(3) &= a_{kN}, & b_{Mk}(3) &= a_{N-2,N-1}a_{N-1,N}a_{Nk}/s \end{aligned} \right\} \quad k \leq M - 1$$

$$s = a_{N-2,N-1}a_{N-1,N} + a_{N-2,N-1}a_{N,N-1} + a_{N,N-1}a_{N-1,N-2}$$

Comparison of the transition fluxes of Eq. (3), expressed in terms of the  $q_k$ , with those of Eq. (6) yields

$$J_{ij} = Y_{ij}(1), \quad i \leq M - 1 \quad \text{and} \quad j \leq M - 1$$

$$\left. \begin{aligned} J_{i,N-2} &= Y_{iM}(1) \\ J_{i,N-1} &= Y_{iM}(2) \\ J_{iN} &= Y_{iM}(3) \end{aligned} \right\} \quad i \leq M - 1 \quad (10)$$

$$J_{N-2,N-1} = J_{N-1,N} = 0, \quad \text{by assumption}$$

Thus, all of these fluxes  $J_{ij}$  are nicely expressed in terms of the  $Y_{kl}(\beta)$ . However, there is one remaining flux in Eq. (3), which is given by

$$J_{N-2,N} = (a_{N,N-1}a_{N-1,N-2}a_{N-2,N} - a_{N,N-2}a_{N-2,N-1}a_{N-1,N})q_M/s \quad (11)$$

As can easily be seen, this flux cannot be expressed in terms of the parameters and variables of Eqs. (4)–(6). Thus, after the elimination of fast-relaxing variables through Eqs. (7) and (8), the fluxes  $J_{ij}$  of Eq. (3) are not completely described by the fluxes  $Y_{kl}(\beta)$  of Eq. (6). This is so, since the assumption that the transition probabilities of Eq. (7) are several orders of magnitude larger than the other  $a_{ij}$  does not in general affect the order of magnitude of  $J_{N-2,N}$ .

For future considerations it is useful to note that the thermodynamic force  $X$  for the net flux around the cycle  $N \rightarrow N - 1 \rightarrow N - 2 \rightarrow N$  is given by<sup>(2,6)</sup>

$$e^{X/kT} = \frac{a_{N,N-1}a_{N-1,N-2}a_{N-2,N}}{a_{N,N-2}a_{N-2,N-1}a_{N-1,N}} \tag{12}$$

where  $k$  is the Boltzmann constant and  $T$  is the temperature in  $K$ . Thus, we may write

$$J_{N-2,N} \propto (e^{X/kT} - 1)q_M \tag{13}$$

### 3.2.

As a second example, let us again consider the case where all  $n_{ij} = 1$ , but we now assume that at least one term in

$$\sum_{\substack{j=1 \\ j \neq N-1}}^N a_{N-1,j}$$

other than  $a_{N-1,N}$  and at least one term in

$$\sum_{j=1}^{N-1} a_{Nj}$$

other than  $a_{N,N-1}$  are several orders of magnitude larger than the other  $a_{ij}$  (with the possible exceptions of  $a_{N,N-1}$  and  $a_{N-1,N}$ ).  $p_N$  and  $p_{N-1}$  are then "transient intermediates"<sup>(2)</sup> and may be eliminated for long times by setting  $\dot{p}_N = \dot{p}_{N-1} = 0$  and using the results to substitute for  $p_N$  and  $p_{N-1}$  in the other  $\dot{p}_i$ . Equation (4) is then obtained with

$$M = N - 2; \quad q_k = p_k, \quad k \leq M; \quad m_{kl} = 5; \quad k \text{ and } l \leq M \tag{14}$$

It is left to the reader to supply the rather involved expressions for the  $b_{kl}(\beta)$ .

On comparison of the  $J_{ij}$  as functions of the  $q_k$  with the  $Y_{kl}(\beta)$ , it is found that all  $J_{ij}$  for  $i$  and  $j \leq M$  may be expressed in terms of the  $Y_{kl}(\beta)$ , but that any of the  $J_{ij}$  for which  $i$  or  $j = N$  or  $N - 1$  involve at least one term of the form

$$J_k^* = (a_{k,N-1}a_{N-1,N}a_{Nk} - a_{kN}a_{N,N-1}a_{N-1,k})p_k/S \tag{15}$$

where

$$S = \left( \sum_{l=1}^M a_{Nl} \right) \left( \sum_{l=1}^M a_{N-1,l} \right) + a_{N,N-1} \left( \sum_{l=1}^M a_{N-1,l} \right) + a_{N-1,N} \left( \sum_{l=1}^M a_{Nl} \right)$$

and

$$1 \leq k \leq M$$

Thus, any of the  $J_{ij}$  which involve state  $N - 1$  or state  $N$  cannot be expressed completely in terms of the  $Y_{kl}(\beta)$ .

In a manner similar to the previous example, we note that

$$J_k^* \propto (e^{X_k^*/kT} - 1)p_k^* \quad (16)$$

where  $X_k^*$  is the thermodynamic force for the net flux around the cycle  $k \rightarrow N - 1 \rightarrow N \rightarrow k$ :

$$e^{X_k^*/kT} = \frac{a_{k,N-1}a_{N-1,N}a_{Nk}}{a_{kN}a_{N,N-1}a_{N-1,k}} \quad (17)$$

### 3.3.

Since the two previous examples have both had all  $n_{ij} = 1$ , we should consider one last simple example with multiple pathways in Eqs. (1)–(3). We take

$$N = 4, \quad n_{12} = n_{34} = 2, \quad n_{13} = n_{24} = 1 \quad (18)$$

and assume that  $1 \leftrightarrow 4$  and  $2 \leftrightarrow 3$  transitions are not allowed. We further assume that transitions  $1 \leftrightarrow 2$  and  $3 \leftrightarrow 4$  by pathway 1 occur by the same process, that the same is true for pathway 2 for these transitions (although pathways 1 and 2 represent different processes), and that transitions  $1 \leftrightarrow 3$  and  $2 \leftrightarrow 4$  also occur by an identical (but distinct from the other two) process. Detailed balance at equilibrium is then satisfied by writing

$$\begin{aligned} a_{34}(1) &= \phi a_{12}(1), & a_{43}(1) &= e^u \phi a_{21}(1) \\ a_{34}(2) &= \phi a_{12}(1), & a_{43}(2) &= e^u \phi a_{21}(2) \\ a_{24} &= \psi a_{13}, & a_{42} &= e^u \psi a_{31} \end{aligned} \quad (19)$$

[Two comments: (i) the stationary state of this example will not be an equilibrium one unless  $a_{12}(1)a_{21}(2) = a_{21}(1)a_{12}(2)$ ; (ii) in general, it would be possible to have distinct  $\phi$ 's for each of the pathways for  $3 \leftrightarrow 4$  transitions; we have assumed  $\phi_1 = \phi_2 = \phi$  for simplicity.]

From Eqs. (1) and (19), we see that  $p_4$  may be eliminated for long times as  $u \rightarrow \infty$ .<sup>(2)</sup> In this limit, upon setting  $\dot{p}_4 = 0$ , we obtain Eq. (4) with

$$\begin{aligned} M &= 3, & q_k &= p_k, & k &\leq 3, & m_{12} &= 2, & m_{13} &= 1, & m_{23} &= 2 \\ b_{kl}(\beta) &= a_{kl}(\beta), & k &= 1, & l &= 2, 3 \\ b_{23}(1) &= \sigma a_{13} a_{21}(1), & b_{32}(1) &= \sigma a_{31} a_{12}(1) \\ b_{23}(2) &= \sigma a_{13} a_{21}(2), & b_{32}(2) &= \sigma a_{31} a_{12}(2) \\ \sigma &= \phi \psi \{ \psi a_{31} + \phi [ a_{21}(1) + a_{21}(2) ] \} \end{aligned} \quad (20)$$

The transition fluxes of Eq. (3) are given adequately for long times in terms of those of Eq. (6) except for

$$\begin{aligned}
 J_{34}(1) &= -Y_{23}(1) + J^*, & J_{34}(2) &= -Y_{23}(2) - J^* \\
 J^* &= \frac{\phi^2 [a_{12}(1)a_{21}(2) - a_{21}(1)a_{12}(2)]}{\psi a_{31} + \phi [a_{21}(1) + a_{21}(2)]} q_3
 \end{aligned}
 \tag{21}$$

As in the other two examples, there is a contribution to some of the  $J_{ij}(\alpha)$  which cannot be expressed in terms of the  $Y_{kl}(\beta)$ . We also note that the missing contribution is related to the thermodynamic force  $X^*$  for the cycle  $3 \xrightarrow{(1)} 4 \xrightarrow{(2)} 3$ :

$$J^* \propto e^{(X^*/kT-1)} q_3
 \tag{22}$$

Because of the simplicity of this example, a further interesting calculation may easily be made. The total net rate of the process by which the transitions  $1 \leftrightarrow 2$  and  $3 \leftrightarrow 4$  occur via pathways (1) is given by

$$J(1) = J_{12}(1) + J_{34}(1)
 \tag{23}$$

Further, we see from Eq. (21) that  $J^*$  contributes to this rate. At the stationary state (in the limit  $u \rightarrow \infty$ ), we find

$$\frac{J^*}{J(1)} = \frac{\phi^2 a_{13} [a_{21}(1) + a_{21}(2)]}{\{\psi a_{31} + \phi [a_{21}(1) + a_{21}(2)]\} (a_{31} + \phi a_{13})}
 \tag{24}$$

As  $\phi$  becomes large, this ratio goes to unity, and  $J^*$ , the flux not obtainable from Eqs. (4)–(6), is the only significant contribution to  $J(1)$ .

#### 4. FLUXES, EQUILIBRIUM AND NONEQUILIBRIUM STATIONARY STATES, AND ENTROPY PRODUCTION

Three examples have been given where the transition fluxes of Eq. (6) corresponding to the dynamical evolution equations (4) do not offer an adequate expression of the transition fluxes of Eq. (3) corresponding to the evolution equations (1) for long times, when Eq. (4) has been obtained from Eq. (1) by the elimination of fast-relaxing variables. In the last example, it was also seen that the missing flux may be the dominant one. With the use of the concept of cycle fluxes<sup>(2,6)</sup> some insight into when this problem arises can now be offered.

On inspection of the kinetic diagrams<sup>(2)</sup> of the dynamical evolution equations (1) and (4) for the three examples, it can be seen that the elimination of fast-relaxing variables has also eliminated cycle(s) from the diagrams. In the first example, the cycle  $N \rightarrow N - 1 \rightarrow N - 2 \rightarrow N$  was

eliminated; in the second, the cycles  $i \rightarrow N - 1 \rightarrow N \rightarrow i$ ,  $i \leq N - 2$ ; and in the third, the cycle  $3 \xrightarrow{(1)} 4 \xrightarrow{(2)} 3$ . We have already noted that, in all three cases, the missing fluxes  $J_{ij}(\alpha)$  which cannot be expressed in terms of the  $Y_{kl}(\beta)$  are proportional to factors of the form  $(e^{X/kT} - 1)$ , where  $X$  is the thermodynamic force for the eliminated cycle [Eqs. (13), (16), and (22)]. Furthermore, we note that the eliminated cycles are represented in the evolution equations (4) by a single state: state  $M$  in the first example; state  $i$ ,  $i \leq M$ , in the second; and state 3 in the third. In fact, if the fluxes for the eliminated cycles are calculated for the stationary state,<sup>(2)</sup> it is seen that the missing fluxes are contributions to the eliminated cycle fluxes in the second and third cases [Eqs. (16) and (22)], and that the missing flux in the first example [Eq. (13)] is identical to the eliminated cycle flux.

It is also to be noted that, if the thermodynamic force for an eliminated cycle vanishes, then the net flux around the cycle vanishes in the stationary state, as do the fluxes  $J_{ij}(\alpha)$  [Eqs. (13), (16), and (22)] which cannot be expressed in terms of the  $Y_{kl}(\beta)$ . Thus, the fluxes  $J_{ij}(\alpha)$  will all be represented adequately for long times by the  $Y_{kl}(\beta)$  if all cycles have zero thermodynamic force and, therefore, the system has an equilibrium stationary state.<sup>(2,6)</sup> On the other hand, the  $Y_{kl}(\beta)$  will not give an adequate representation of the  $J_{ij}(\alpha)$  if an eliminated cycle has a nonzero thermodynamic force and the system has a nonequilibrium stationary state.

It is reasonable to speculate that it is always the case that the  $Y_{kl}(\beta)$  do not yield an adequate representation of the  $J_{ij}(\alpha)$  when the elimination of fast-relaxing variables which leads from Eq. (1) to Eq. (4) eliminates a cycle with nonzero thermodynamic force. Let us consider a two-state cycle such as that between states 3 and 4 in the third example. If all of the transition probabilities for this cycle are several orders of magnitude larger than the other  $a_{ij}(\alpha)$ , then one may write for long times<sup>(2,3)</sup>

$$[a_{34}(1) + a_{34}(2)]p_3 = [a_{43}(1) + a_{43}(2)]p_4 \quad (25)$$

Upon definition of a new state of probability  $p_3 + p_4$ , Eqs. (4)–(6) are obtained with the cycle represented only by the new state. Thus, the cycle has been eliminated. However, it may be precisely because of fast fluxes around the cycle that Eq. (25) obtains, and these fluxes will not appear in Eqs. (4)–(6). If, on the other hand, the probability of state 4 may be eliminated because  $a_{43}(2)$ , say, is much larger than  $a_{34}(1)$ ,  $a_{34}(2)$ , and  $a_{24}$ , then the cycle is again eliminated. However, it is not implied that there is no flux through state 4, but rather, that if state 4 is reached, it relaxes very quickly to state 3 via pathway (2). Thus, if state 4 is reached from state 3 via pathway (1), it is highly likely that a turn around the eliminated cycle in



the direction  $3 \xrightarrow{(1)} 4 \xrightarrow{(2)} 3$  is completed. It is precisely a contribution to this cycle flux which is not represented in the  $Y_{kl}(\beta)$ .

Since it has been argued that the  $Y_{kl}(\beta)$  will not provide a complete description of the  $J_{ij}(\alpha)$  only when an eliminated cycle has a nonzero thermodynamic force, a small point regarding the Glansdorff–Prigogine stability criterion,<sup>(7)</sup> that the second-order variation of the entropy production around the stationary state be positive, is in order in the context of systems with nonequilibrium stationary states. From Schnakenberg's work,<sup>(6)</sup> we know that both Eqs. (1) and (4) satisfy this stability criterion. For the three examples considered, it can easily be shown that the entropy production ( $P$ ) of Eq. (1) is related to that ( $Q$ ) of Eq. (4) by  $P = Q + P^*$ , where  $P^*$  is the entropy production corresponding to the fluxes not represented in Eqs. (4)–(6). It can further be shown that  $P^*$  is of the general form  $\sum_i \rho_i p_i$ , where the  $\rho_i$  are independent of the  $p_i$ . Thus, the second-order variation of  $P^*$  around the stationary state,  $\delta^2 P^* = 0$ , so that  $\delta^2 P \doteq \delta^2 Q$ .

This result is actually to be expected, since entropy production may be considered as the sum of a contribution due to changes in the internal state of the system and another due to coupling to reservoirs. It is the former which is decisive for the stability criterion, and it is the contribution which is due to population properties, which are adequately described by both Eqs. (1) and (4). The entropy production corresponding to those fluxes not represented in Eqs. (4)–(6), however, is part of that due to coupling to reservoirs. It is this coupling which allows for nonequilibrium stationary states.

## 5. DISCUSSION

It is generally presumed that dynamical evolution equations of the form of Eq. (1) offer a complete description of a system, in that Eq. (1) itself describes the population properties and the fluxes of Eq. (3), which are deduced from Eq. (1) with the help of Eq. (2), offer a description of the rates of processes occurring in the system. However, we have demonstrated that this is not necessarily the case. The dynamical evolution equations (4), which are obtained from Eq. (1) by the elimination of fast-relaxing variables, are of the form of Eq. (1), but the fluxes of Eq. (6) corresponding to Eq. (4) may not describe the fluxes of Eq. (3) adequately. In each case, the fluxes are defined from the evolution equations in a self-consistent manner. It can also be said that each case is thermodynamically consistent regarding its entropy production and second-order variation thereof. However, even though Eqs. (4)–(6) are obtained from Eqs. (1)–(3) in a manner which ensures that they are mutually consistent regarding population properties

and the Glansdorff-Prigogine stability criterion for long times, they may not be mutually consistent regarding fluxes and entropy production if the elimination of fast-relaxing variables also leads to the elimination of a cycle with nonzero thermodynamic force.

Only rarely does one have available evolution equations which detail all the possible states of a system and whose corresponding fluxes would thus be ensured of giving a complete description of the rates of all processes occurring in the system. As pointed out by Schnakenberg<sup>(6)</sup> for master equations, the states considered are usually the result of a coarse-graining procedure. In fact, in some disciplines (e.g., biochemistry<sup>(8)</sup>), coarse-grained descriptions are the ones of interest. In the terms of this work, most dynamical evolution equations are the result of the elimination of fast-relaxing variables. Thus, if the system under consideration has a nonequilibrium stationary state, one is not assured that the fluxes corresponding to the evolution equations offer a complete description of the rates of processes occurring in the system.

There is a point of view that would say that any elimination which leads to an incomplete description of the rates of processes is simply invalid. However, this point of view ignores the considerations of the preceding paragraph, that the most detailed description available usually is already the result of several eliminations of fast-relaxing variables. It could further be argued, though, that as better experimental techniques are developed, more states of the system would be recognized, until, in principle at least, one could eventually have a description detailing all states of the system. The fluxes corresponding to the evolution equations at this level would then offer a complete description of the rates of processes occurring in the system. This argument assumes, however, that the system under consideration belongs to what Elsasser<sup>(9)</sup> has called an "infinite universe of discourse." For a "finite universe of discourse," to which many biological systems, for example, may belong, there are many more quantum states available to the system than there are realizations of the system. For such systems, a description detailing all quantum states may not be attainable. It would not then be possible to obtain a quantum level evolution equation, whose corresponding fluxes would be assured of giving a complete description of the rates of all processes.

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