

# Fluctuations Around Nonequilibrium States in Open Nonlinear Systems

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The theory of nonequilibrium fluctuations in open systems is extended to nonlinear situations. It is shown that the usual birth-and-death type of stochastic formulation of chemical kinetics is in general inadequate and has to be replaced by a more detailed phase-space description. As a consequence, for large classes of nonlinear systems arbitrarily far from equilibrium, the classical Einstein fluctuation formula can be extended, provided the steady reference state is asymptotically stable. The case of oscillatory or unstable systems is also discussed. It is conjectured that in such systems, the departure from the steady state is governed by large fluctuations of "macroscopic" size, while small fluctuations are still described by the extended Einstein formula. Nonequilibrium macroscopic instabilities such as chemical or hydrodynamic instabilities seem therefore to bear strong similarities to first-order phase transitions.

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**KEY WORDS:** Fluctuations; instabilities; thermodynamics of irreversible processes; stochastic processes; master equations; ecology; chemical kinetics.

## 1. INTRODUCTION

Recent advances in irreversible thermodynamics have drawn attention on some general and unexpected features of steady nonequilibrium states.<sup>(1)</sup> Of particular interest for the present investigation is the observation that in

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nonlinear systems the stability of such states may be compromised and the system can subsequently evolve to a new regime showing spatial, temporal, or functional organization. Hydrodynamic instabilities have long been known to give rise to this phenomenon. It is now well-established that, unexpectedly, in purely dissipative systems such as open systems undergoing certain types of chemical reactions, the steady nonequilibrium states may also become unstable and a new type of *dissipative structure* may emerge beyond instability.<sup>2</sup>

The universality of instabilities in macroscopic physics and the importance of the new regime beyond the transition in fluid dynamics, physical chemistry, and biology are sufficient to justify the interest for studying the behavior of fluctuations around nonequilibrium states in nonlinear systems.<sup>3</sup> Such a study is indeed a necessary prerequisite to a real understanding of the mechanism of setting up an instability and of the evolution of the system to the new macroscopic state beyond instability. In many treatments, fluctuations are *introduced a priori* in the macroscopic equations of evolution. This procedure, however, compromises from the very beginning the possibility to really understand the *emergence* of fluctuations. In addition, especially in nonlinear systems, it may give rise to inconsistencies related to the time scale of variation of the fluctuations. It follows that a satisfactory theory of nonequilibrium fluctuations must be based on statistical mechanics or at least on the theory of stochastic processes.

As a first step in this program, the nonequilibrium fluctuations in open chemical systems have been studied recently<sup>(3)</sup> in an approach based on the stochastic theory of chemical kinetics, a very clear presentation of which is available.<sup>(4)</sup> As explained in Ref. 3, the choice of chemical kinetic models was motivated by the simplicity of the mathematical formulation due to the discrete character of the stochastic variable and by the fact that, by varying the affinities, one can obtain situations very far from equilibrium, including the possibility for unstable transitions.

The main conclusion of the Nicolis–Babloyantz analysis<sup>(3)</sup> is that in the most general sequence of monomolecular reactions in ideal mixtures arbitrarily far from equilibrium, the probability of fluctuations around the steady state<sup>4</sup> of the number of particles of an intermediate component  $X$  is given by a Poisson distribution. Alternatively, in the limit of small fluctuations, one obtains a Gaussian distribution which is shown to reduce to the form

$$P(\delta X) \propto \exp[(\delta^2 S)_0/2k] \quad (1)$$

<sup>2</sup> For a general review see Ref. 1.

<sup>3</sup> The present paper gives the details of the calculation of the stochastic approach to the fluctuations far from equilibrium. Most of the general ideas have been given earlier.<sup>(2a, b)</sup>

<sup>4</sup> In the models studied in Ref. 3 the steady nonequilibrium states are stable with respect to arbitrary perturbations.

where  $\delta X = X - X_0$ ,  $X_0$  being the value of  $X$  at the steady nonequilibrium state,  $k$  is Boltzmann's constant, and  $\frac{1}{2}(\delta^2 S)_0$  is the second-order excess entropy evaluated around the steady state. Equation (1) shows that for the linear, stable modes studied in Ref. 3 the classical Einstein equilibrium formula<sup>(1,3)</sup> can be extended, provided one uses suitable steady-state parameters rather than equilibrium quantities. An important consequence is that in an ideal reacting mixture, the mean quadratic fluctuations are still given by an extension of the well-known thermodynamic expression

$$\overline{\delta X^2} = \bar{X} = X_0 \quad (2)$$

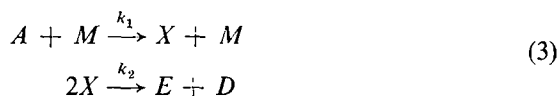
Similar results have been derived in Refs. 5-8. The particular models studied in Refs. 7a, b and 8 dealt with current fluctuations in electrical circuits. The case of nonequilibrium chemical kinetics has been considered in Ref. 5. Another class of situations for which the equilibrium Einstein theory can be extended refers to systems which are close to thermodynamic equilibrium.<sup>(4,6,8)</sup>

The object of the present paper is to present the details of the analysis of fluctuations in nonlinear systems far from equilibrium as outlined in recent papers by Prigogine and the author.<sup>(2a,b)</sup> In Section 2, we consider a simple nonlinear chemical model involving a single bimolecular step. Assuming that the macroscopic mass-conservation equations define a Markovian process in the number-of-particles space, we derive a stochastic master equation in this space using the methods of Refs. 3 and 4. Surprisingly, this equation leads to results which, far from equilibrium, are different from (1) and (2) and seem to imply that in nonlinear systems, the behavior of fluctuations depends strongly on the detailed properties of the individual kinetic steps. On the other hand, a number of general arguments indicate (details are given in Section 2) that in the whole range of *local equilibrium theory* in which local thermodynamic variables may be used to describe irreversible processes,<sup>(1,3,9)</sup> Eq. (1) remains valid. Now, in a system of chemical reactions, local equilibrium is usually attained because of the frequent *elastic* collisions with a solvent or with an inert component of the gaseous mixture. This suggests that a proper description of fluctuations requires the details of the microscopic behavior of the system as given, e.g. by a kinetic equation of the Boltzmann type. Assuming that this equation defines a Markovian process in the *complete* phase space (including internal states of individual molecular species), we derive in Section 3 a generalized master equation in this space following a method due to Siegert. The result is that Eqs. (1) and (2) are recovered as consistent approximations in the limit of dilute mixtures. The conclusion is thus drawn that in nonlinear systems the usual birth-and-death type of stochastic approach is inadequate and a satisfactory description must be based on a phase space analysis.

As a preliminary to the problem of fluctuations around instabilities, the Volterra–Lotka model is studied in Sections 4 and 5 in its chemical kinetic and its ecological versions. The phase space analysis shows that small thermal fluctuations obey Eqs. (1) and (2). However, the system may evolve from the steady state by a mechanism of *large* (macroscopic) fluctuations which drive the average values to a time-dependent regime. The usual birth-and-death type of stochastic analysis predicts a very different behavior: Small fluctuations increase with time and, stochastically, the steady state is never stable. According to Section 2, the latter possibility has to be ruled out in chemical kinetics. However, in an ecological system, both the regime predicted by the phase space and the usual stochastic description are possible and correspond to different types of situations. Section 6 is devoted to some comments concerning the mechanism of setting up a macroscopic instability in a dissipative system and the implications of the results of Sections 3 and 5 in nonlinear thermodynamics of irreversible processes,

## 2. A SIMPLE NONLINEAR MODEL

The main ideas of this section will be illustrated on the simple bimolecular scheme:



A slightly different version of this scheme has already been considered in Ref. 3. The system is open to large reservoirs of  $A$ ,  $M$ ,  $E$ ,  $D$ . Inverse reaction rates are neglected. The system thus operates automatically far from thermodynamic equilibrium. The overall reaction is



and the macroscopic chemical kinetic equations read, for an ideal mixture,

$$dX/dt = k_1AM - 2k_2X^2, \quad A, M = \text{const} \quad (4a)$$

The system admits a single steady state

$$X_0 = (k_1AM/2k_2)^{1/2} \quad (4b)$$

which is asymptotically stable with respect to arbitrary perturbations.

In the macroscopic description, Eqs. (4a)–(4b), fluctuations are neglected. We now adopt a more refined description and assume that (4a) define a Markovian stochastic process in the space of the total numbers of particles of the constituents  $A$ ,  $M$ ,  $D$ ,  $E$ ,  $X$ . In chemical kinetics, it is usually

implied that these variables provide a consistent description, independent of the details of the dynamics in momentum space.<sup>(4)</sup> The system is now described in terms of a function  $P(A, M, D, E, X, t)$  which gives the probability for finding given values of the particle numbers at time  $t$ . The equation of evolution for this function (master equation) was established and solved approximately in Ref. 3. In the reduced form where a summation over the reservoir variables is performed, the result reads<sup>(3)</sup> (the system is assumed to remain spatially uniform):

$$dP(X, t)/dt = k_1AMP(X - 1, t) - k_1AMP(X, t) + k_2(X + 1)(X + 2)P(X + 2, t) - k_2X(X - 1)P(X, t) \quad (5)$$

where  $A, M$  are now the average values of the number of particles of  $A, M$  over the reservoir distribution.<sup>5</sup>

It is instructive to study the solutions of Eq. (5) in the limit of small fluctuations. Following van Kampen,<sup>(10)</sup> we express this limit by setting

$$X = \bar{X} + \epsilon x, \quad \epsilon \propto |x/\bar{X}| \ll 1 \quad (6)$$

where  $\bar{X}$  is a macroscopic regime close to or at the steady state (4b) and  $x$  is a random fluctuation. Expanding consistently both  $P$  and the coefficients in Eq. (5) in powers of  $\epsilon$ , we obtain, to the first nontrivial order, a Fokker-Planck equation of the form

$$\frac{\partial P(x, t)}{\partial t} = 4\bar{X} \frac{\partial}{\partial x} xP(x, t) + \left( \frac{k_1AM}{2k_2} + 2\bar{X}^2 \right) \frac{\partial^2 P(x, t)}{\partial x^2} \quad (7)$$

For fluctuations around the steady state,  $\bar{X} = X_0$ . Equation (7) then admits a time-independent solution whose second moment is easily seen to be

$$\overline{\delta X^2} = [(k_1AM/k_2) + 4X_0^2]/8X_0 = \frac{3}{4}X_0 \quad (8)$$

Clearly, Eq. (8) is incompatible with a Poisson distribution and therefore also with (1) and (2). The factor  $\frac{3}{4}$  in front of  $X_0$  is model-dependent. The fluctuations in many other nonlinear models have been tested by the same method. An example is reported in the appendix. The general answer was a non-Poisson distribution with mean quadratic fluctuations depending on the individual kinetic steps. Thus no general statement comparable to Eq. (2) seems to be compatible with the master equation for the probability distribution.

\* Equation (5) implies the validity of a decoupling procedure discussed in detail in Ref. 3. According to this assumption the reservoir state is assumed to vary in a different scale than the state of the subsystem ( $X$ ).

In Ref. 3, the model discussed in this section was studied in the generating function representation. Defining<sup>(4)</sup>

$$f(s_X, t) = \sum_{X=0}^{\infty} s_X^X P(X, t) \quad (9)$$

one obtains from (5) the following equation for  $f$ :

$$\partial f / \partial t = k_1 A M (s_X - 1) f + k_2 (1 - s_X^2) (\partial^2 f / \partial s_X^2) \quad (9a)$$

This equation admits the approximate solution

$$f(s_X, t) = \exp[X_0(s_X - 1)] [1 + \frac{1}{2} X_0 (s_X - 1) - \frac{1}{2} X_0^2 (s_X - 1)^2 + \dots] \quad (9b)$$

In Ref. 3, the quadratic and subsequent terms in  $(s_X - 1)$  in the r.h.s. of this relation were neglected. The remaining terms produced the result (2) for small fluctuations and a distribution for  $X$  which was of the Poisson form. It is easily seen, however, by inverting Eq. (9b) to the corresponding form for  $P(X)$  that the linear term in  $(s_X - 1)$  in Eq. (9a) does not constitute a consistent approximation.<sup>6</sup> When the subsequent terms are taken into account, the result (2) is no longer valid and one again obtains Eq. (8), which is incompatible with a Poisson distribution or with Eq. (1).

Is it possible to accept this conclusion for an ideal mixture of chemically reacting components? The following argument shows that such a result cannot be valid. Consider a classical system of  $\rho$  components and let  $N_{\mathbf{r}\mathbf{p}}^\gamma d\mathbf{r} d\mathbf{p}$  be the number of particles of component  $\gamma$  in a phase space volume element  $d\mathbf{r} d\mathbf{p}$  around a value  $\mathbf{p}$  of the momentum and  $\mathbf{r}$  of the position in space ( $\gamma = 1, \dots, \rho$ ). By definition

$$N_{\mathbf{r}\mathbf{p}}^\gamma = \sum_{1 \leq i_\gamma \leq N_\gamma} \delta(\mathbf{r} - \mathbf{r}_{i_\gamma}) \delta(\mathbf{p} - \mathbf{p}_{i_\gamma}) \quad (10)$$

Because of the intermolecular interactions, the functions  $N_{\mathbf{r}\mathbf{p}}^\gamma$  are, for fixed values of  $\mathbf{r}$  and  $\mathbf{p}$ , random functions of the time. Let  $P(\{N_{\mathbf{r}\mathbf{p}}^\gamma\}, t)$  be the distribution function for the different values of  $N_{\mathbf{r}\mathbf{p}}^\gamma$ . Denoting by a bar the average over this distribution, one can derive the following general identities<sup>7 (11)</sup>:

$$\overline{N_{\mathbf{r}\mathbf{p}}^\gamma(t)} = F_1^\gamma(\mathbf{r}, \mathbf{p}, t) \quad (11a)$$

$$\overline{\delta N_{\mathbf{r}\mathbf{p}}^\gamma(t) \delta N_{\mathbf{r}'\mathbf{p}'}^\gamma(t)} = \delta(\mathbf{r} - \mathbf{r}') \delta(\mathbf{p} - \mathbf{p}') \delta_{\gamma\gamma'}^{K\gamma} F_1^\gamma(\mathbf{r}, \mathbf{p}, t) + G_{12}^{\gamma\gamma'}(\mathbf{r}, \mathbf{r}', \mathbf{p}, \mathbf{p}', t) \quad (11b)$$

<sup>6</sup> Thus the final equation (3.24) of the Nicolis-Babloyantz paper<sup>(3)</sup> is wrong, although the analysis of Section III and the approximate result (3.22) are correct.

<sup>7</sup> Similar relations are used in the theory of point processes, e.g., cascade processes. For a detailed discussion, see Bharucha-Reid, Ref. 4, Ch. 5.

Here  $F_1^\gamma$  denotes the singlet Boltzmann density distribution function,  $G_{12}^{\gamma\gamma'}$  the two-particle correlation function, and  $\delta N_{rp}^\gamma$  is an excess variable defined as  $\delta N_{rp}^\gamma = N_{rp}^\gamma - \bar{N}_{rp}^\gamma$ .

Let us consider Eqs. (11a)-(11b) in the limit of a dilute mixture. In general, both  $F_1$  and  $G_{12}$  are complicated functionals of the interactions and of the number densities through the kinetic equations describing their time evolution. Here, we are especially interested in systems described by a *local equilibrium theory*, in which the state functions such as entropy density are described locally by the same variables as in equilibrium and depend on time implicitly, through these local variables. A sufficient condition for the validity of this theory is that the distribution functions of velocities and relative positions deviate only slightly from their local equilibrium forms<sup>(1,9)</sup>  $F_1^{\gamma(0)}$ ,  $G_{12}^{\gamma\gamma'(0)}$ . Setting

$$F_1^\gamma \simeq F_1^{\gamma(0)} = \text{local Maxwellian} = O(n_\gamma) \tag{12a}$$

one obtains

$$G_{12}^{\gamma\gamma'} \simeq O(n_\gamma n_{\gamma'}) \tag{12b}$$

$n_\gamma$  being the number density of component  $\gamma$  ( $n_\gamma \ll 1$  in dilute systems). It follows that in a dilute mixture, Eq. (11b) becomes

$$\overline{\delta N_{rp}^\gamma(t) \delta N_{r'p'}^{\gamma'}(t)} = \delta(\mathbf{r} - \mathbf{r}') \delta(\mathbf{p} - \mathbf{p}') \delta_{\gamma\gamma'}^{kr} F_1^\gamma + O(n^2) \tag{13}$$

Integrating over  $\mathbf{r}$ ,  $\mathbf{r}'$ ,  $\mathbf{p}$ ,  $\mathbf{p}'$ , we obtain

$$\overline{\delta \mathcal{N}^\gamma \delta \mathcal{N}^{\gamma'}} = \delta_{\gamma\gamma'}^{kr} \mathcal{N}^\gamma + O(\mathcal{N}^\gamma n_{\gamma'}) \simeq \delta_{\gamma\gamma'}^{kr} \mathcal{N}^\gamma \tag{14}$$

$\mathcal{N}^\gamma$  being the number of particles of constituent  $\gamma$  in the volume  $V$ . Equation (14) has the same structure as the generalized Einstein relation (2) and indicates that, in contrast to the result given in Eq. (8), in a local equilibrium theory, the mean square fluctuations in a dilute system are given by a universal expression independent of the particular model.

It is not difficult to see that the discrepancy between this general argument and the analysis based on the usual stochastic master equations of the type studied in this section is due to the fact that for nonlinear systems, the stochastic description in the space of the total numbers of particles is inadequate. The difficulty becomes particularly transparent in the case of a local equilibrium theory. In a dynamical system, such as a dilute reactive mixture, local equilibrium is secured by the frequent elastic collisions with a dense inert component. The latter restore continuously an average Maxwellian distribution which otherwise would be perturbed by the reactive collisions. Now this

dynamical process involves *two largely separated time scales*: the relaxation time between elastic collisions, which is a very short time, and the macroscopic scale over which the chemical composition changes as a result of reactive collisions. The effects related to the relaxation time are fundamentally microscopic and cannot be accounted for correctly in a description where the internal states (e.g., the values of the momentum) of the molecules are discarded. We are thus led to the conclusion that in a realistic chemical kinetic problem, fluctuations must be discussed on the basis of a kinetic equation such as the Boltzmann equation containing both reactive and elastic collisions, rather than in terms of the macroscopic chemical kinetic equation (4) in which the effects referring to the fast time scale have been averaged.<sup>8</sup> It is only in the limit of linear systems or of systems close to equilibrium, in which fluctuations involve a single time scale, that the two approaches become compatible. The condition that the stochastic master equations for fluctuations should be compatible with the Boltzmann equation is also stated in a paper by Oppenheim *et al.*,<sup>(12)</sup> who, however, did not carry further the consequences of this remark.<sup>9</sup>

### 3. PHASE-SPACE DESCRIPTION OF FLUCTUATIONS

Let us now outline briefly the theory of fluctuations for model (3) starting from a kinetic equation description in phase space. As we deal with dilute mixtures, the equation will reduce to the usual Boltzmann form. We adopt the notation  $\bar{F}_\alpha^\gamma$  for the Boltzmann probability density of component  $\gamma$  corresponding to an internal state  $\alpha$  and assume for simplicity that the spectrum of  $\alpha$  is discrete. The bar over  $F_\alpha^\gamma$  reminds us that in the Boltzmann equation description,  $\bar{F}_\alpha^\gamma$  represents an *average* quantity. Bearing this in mind, one can easily write the Boltzmann equation corresponding to model (3)<sup>(13)</sup>:

$$d\bar{F}_\alpha^X/dt = \sum_{jkl} B_{jka\ell} \bar{F}_j^A \bar{F}_k^M - 2 \sum_{jkl} A_{\alpha jkl} \bar{F}_\alpha^X \bar{F}_j^X + (d\bar{F}_\alpha^X/dt)_{e1} \quad (15)$$

In the r.h.s. of this equation,  $(d\bar{F}_\alpha^X/dt)_{e1}$  describes the effect of elastic collisions and the remaining two terms refer to reactive collisions.  $B_{ijkl}$  and  $A_{ijkl}$  are the transition probabilities per unit time for scattering between two molecules in states  $(ij)$  into two molecules in states  $(kl)$  for the reactions corresponding

<sup>8</sup> The change of character of a stochastic process induced by a contraction in the description is a well-known phenomenon in stochastic theory (see, e.g., Kac, Ref. 14a).

<sup>9</sup> The inadequacy of the birth-and-death process formulation has long been recognized in the theory of cascade processes. See, e.g., Bharucha-Reid, Ref. 4, Ch. 5.



to the two steps in (3). They satisfy a number of conditions imposed by the mechanics of a scattering process:

$$\begin{aligned}
 A_{ii,kl} &= 0 \\
 A_{ij,kl} &= A_{ji,kl} = A_{ij,lk} \geq 0 \quad \text{for } (kl) \neq (ij) \\
 \sum_{kl} A_{ij,kl} &= 0
 \end{aligned}
 \tag{16a}$$

If one requires in addition microscopic reversibility, we have

$$A_{ij,kl} = A_{kl,ij} \tag{16b}$$

The system is again assumed to remain uniform. The factor two in front of the quadratic term in  $\bar{F}^X$  expresses the fact that the population of  $X$  in the  $\alpha$  state may be decreased in two ways, corresponding to either of the two  $X$  molecules in the second step of (3) being in the energy level  $\alpha$ .

We now place ourselves in the limit of very frequent elastic collisions. According to our previous remarks, this implies

$$\bar{F}_\alpha^X \sim \bar{F}_\alpha^{X(0)} = \text{local Maxwellian} \tag{17a}$$

and similarly for  $A, M, D, E$ ; i.e.,

$$(d\bar{F}_\alpha^X/dt)_{el} \simeq 0 \tag{17b}$$

We are thus permitted to neglect the explicit effect of elastic collisions in the kinetic equation. Of course, the influence of these collisions remains implicitly in the reactive terms through the fact that the molecular speed distributions are now Maxwellian and that distinction is made between molecules occupying different momentum states. In fact, Eqs. (15) and (17) now express that, as a rule, the system remains stationary on the microscopic scale because of the frequent elastic collisions, but from time to time, it is slightly perturbed by reactive collisions between molecules which are sufficiently energetic to overcome the potential barrier for binding. In a sense, reactive collisions are “exceptional” events associated with the tail of the Maxwellian velocity distribution.

Let us set  $\bar{F}_\alpha(\Delta\mathbf{r} \Delta\mathbf{p})_\alpha = \bar{f}_\alpha$ , with  $\bar{f}_\alpha$  the average number of molecules in the phase-space volume  $(\Delta\mathbf{r} \Delta\mathbf{p})_\alpha$  around  $(\mathbf{r}_\alpha, \mathbf{p}_\alpha)$ . In the kinetic equation description the fluctuations of  $f_\alpha$  around this average are neglected. We now go to a more refined description in terms of the probability for having, at time  $t$ , given occupation numbers for the various internal states. An equation of evolution for this function may be derived by assuming that Eq. (15) defines a Markov process in the complete phase space. The procedure is quite similar to that leading to equations of the type (5) and has been discussed in detail by Kac and Siegert.<sup>(14)</sup> One obtains, straightforwardly, a reduced

equation of evolution for the distribution of  $f^X$  summed over the reservoir variables:

$$\begin{aligned}
 dP(\{f^X\}, t)/dt = & \sum_{ijkl} B_{ijkl} \bar{f}_i^A \bar{f}_j^M [P(f_k^X - 1, \{f'\}, t) - P(f_k^X, \{f'\}, t)] \\
 & + \sum_{ijkl} A_{ijkl} [(f_i^X + 1)(f_j^X + 1) P(f_i^X + 1, f_j^X + 1, \{f'\}, t) \\
 & - f_i^X f_j^X P(f_i^X, f_j^X, \{f'\}, t)] \quad (18)
 \end{aligned}$$

Here,  $\{f'\}$  denotes the occupation numbers of the states which are not implied in the reaction steps. It is easily verified that when Eq. (18) is multiplied by  $f_k^X$  and averaged over all  $f$ 's, it yields Eq. (15) provided a factorization assumption is made on  $P$ . We shall come back to this point later in this section. Finally, it should be pointed out that the reduced equation (18) is obtained from a more general master equation involving fluctuations of the reservoir composition, by summing over the reservoir variables and assuming that the latter vary over a different time scale compared to the variables of the subsystem corresponding to constituent  $X$ . The validity of this *decoupling assumption* is discussed in detail in Ref. 3.

The difficulty in solving Eq. (18) arises from the infinite number of coupled terms contained in the two sums over internal states in the r.h.s. For this reason, we shall presently study this equation in the limit of small fluctuations. As in Eq. (6), we express this limit by setting

$$f_k^X = \bar{f}_k^X + \delta f_k^X = \bar{f}_k^X + \epsilon x_k, \quad \epsilon \propto |x_k| \bar{f}_k^X \ll 1 \quad (19)$$

where the deviations  $x_k$  are now due to thermal fluctuations.

Expanding consistently both  $P$  and the coefficients in Eq. (18) in powers of  $\epsilon$  and keeping the dominant terms, we obtain

$$\begin{aligned}
 \frac{\partial P(\{x\}, t)}{\partial t} = & \sum_{ijkl} B_{ijkl} \bar{f}_i^A \bar{f}_j^M \frac{1}{2} \frac{\partial^2 P}{\partial x_k^2} \\
 & + \sum_{ijkl} A_{ijkl} \left[ \bar{f}_j^X \frac{\partial}{\partial x_i} x_i P + \bar{f}_i^X \frac{\partial}{\partial x_j} x_j P \right. \\
 & \left. + \bar{f}_i^X x_j \frac{\partial P}{\partial x_i} + \bar{f}_j^X x_i \frac{\partial P}{\partial x_j} \right] \\
 & + \sum_{ijkl} A_{ijkl} \bar{f}_i^X \bar{f}_j^X \frac{1}{2} \left[ \frac{\partial^2 P}{\partial x_i^2} + \frac{\partial^2 P}{\partial x_j^2} + 2 \frac{\partial^2 P}{\partial x_i \partial x_j} \right] \\
 & + \sum_{ijkl} A_{ijkl} \bar{f}_i^X \bar{f}_j^X \left( \frac{\partial P}{\partial x_i} + \frac{\partial P}{\partial x_j} \right) \\
 & - \sum_{ijkl} B_{ijkl} \bar{f}_i^A \bar{f}_j^M \frac{\partial P}{\partial x_k} \quad (20)
 \end{aligned}$$

The last two terms in this equation vanish provided  $\bar{f}^X$  is taken to satisfy the kinetic equation (15) at the steady state. This is consistent with the limit of small fluctuations considered in this section: any deviation of  $\bar{f}^X$  from the nonfluctuating regime described in Eq. (15) introduces in Eq. (20) higher-order terms in  $\epsilon$ .

The simplified equation (20) is now integrated over all  $x$ 's but one. Setting

$$P_{1\dots s}(x_1, \dots, x_s, t) = \int dx_{s+1} \dots dx_{\mathcal{M}} P(\{x\}, t) \tag{21}$$

and taking into account relations (16a) we obtain

$$\begin{aligned} \frac{\partial P_1(x_\alpha, t)}{\partial t} &= \frac{1}{2} \sum_{ijl} B_{ij\alpha l} \bar{f}_i \bar{f}_j^M \frac{\partial^2 P_1(x_\alpha, t)}{\partial x_\alpha^2} \\ &- \sum_{jkl} A_{\alpha jkl} \bar{f}_\alpha \bar{f}_j^X \frac{\partial^2 P_1(x_\alpha, t)}{\partial x_\alpha^2} + 2 \sum_{jkl} A_{\alpha jkl} \bar{f}_j^X \frac{\partial}{\partial x_\alpha} x_\alpha P_1(x_\alpha, t) \\ &- 2 \sum_{jkl} A_{\alpha jkl} \bar{f}_\alpha^X \int dx_j x_j \frac{\partial P_{12}(x_\alpha, x_j, t)}{\partial x_\alpha} \end{aligned} \tag{22}$$

We see that Eq. (20) gives rise to a hierarchy of equations relating

$$\partial P_1(x_\alpha, t) / \partial t \text{ to } P_{12}(x_\alpha, x_j, t)$$

and similarly  $\partial P_{12} / \partial t$  to  $P_{123}$ , etc. It is easy to see, however, that this hierarchy may be decoupled into separate component equations provided a factorization assumption is made on the initial-state reduced probability functions  $P_{1\dots s}(\{f_\alpha\}, t = 0)$ :

$$P_{1\dots s}(\{f_\alpha\}, 0) = \prod_{i=1}^s P_1(f_i, 0), \quad s \ll X \tag{23}$$

Indeed, Eq. (18) has a very similar form to the quantum mechanical Pauli equation in the second quantization representation.<sup>(15)</sup> The interaction operator appearing in this equation has the structure of a diagonal fragment<sup>(15)</sup> in the sense that it connects two states without spatial correlations between particles. In addition, correlations arising from statistics are absent in Eq. (18), which refers to a classical mechanical system. We conclude therefore that the interaction operator in Eq. (18) propagates the factorization property to terms of the order  $1/V$ ,  $V$  being the volume occupied by the system:

$$P_{1\dots s}(\{f_\alpha\}, t) = \prod_{i=1}^s P_1(f_i, t) \tag{24}$$

This equation, together with the definition (19) of the fluctuations  $x_j$ , implies that the last term in Eq. (22) vanishes. The coefficients of the second deriva-

tive  $\partial^2 P_1 / \partial x_\alpha^2$  of this equation may be further simplified by assuming again, consistently with the Fokker-Planck approximation, that the averages  $\bar{f}_j^X$  satisfy the Boltzmann equation (15). One finally obtains the simplified form

$$-\frac{\partial P_1(x_\alpha, t)}{\partial t} = 2 \left( \sum_{jkl} A_{\alpha jkl} \bar{f}_j^X \right) \frac{\partial}{\partial x_\alpha} x_\alpha P_1(x_\alpha, t) + \frac{\partial^2 P_1(x_\alpha, t)}{\partial x_\alpha^2} 2 \bar{f}_\alpha^X \sum_{jkl} A_{\alpha jkl} \bar{f}_j^X \quad (25)$$

This equation has a very similar structure to the usual Fokker-Planck equation of Brownian motion theory with a friction coefficient  $\zeta$  and a diffusion coefficient  $\mathcal{D}$  given by the relations

$$\begin{aligned} \zeta_\alpha &= 2 \sum_{jkl} A_{\alpha jkl} \bar{f}_j^X \\ \mathcal{D}_\alpha &= 2 \bar{f}_\alpha^X \sum_{jkl} A_{\alpha jkl} \bar{f}_j^X \end{aligned} \quad (26)$$

We observe that  $\zeta_\alpha > 0$ . As a result, the steady-state solution of (25) exists and is always stable.<sup>10</sup> To determine its explicit form, it will be sufficient to solve the equation  $\partial P_1(x_\alpha, t) / \partial t = 0$ , i.e.,

$$(\partial / \partial x_\alpha) x_\alpha P_1(x_\alpha) - \bar{f}_\alpha^X [\partial^2 P_1(x_\alpha) / \partial x_\alpha^2] = 0 \quad (27)$$

Note that the transition probability per unit time  $A_{\alpha jkl}$  cancels in the steady state. Equation (27) admits the solution

$$P_1(x_\alpha) = (2\pi \bar{f}_\alpha^X)^{-1/2} \exp(-x_\alpha^2 / 2 \bar{f}_\alpha^X) \quad (28)$$

with

$$(\overline{\delta f_\alpha^X})^2 =: \bar{f}_\alpha^X \quad (29)$$

In Eq. (29),  $\delta f_\alpha^X$  stands for the fluctuations in the number of particles in state  $\alpha$ . In terms of the Boltzmann probability densities, Eq. (29) takes the form

$$\overline{\delta F_\alpha^X(\Delta \mathbf{r} \Delta \mathbf{p})_\alpha \delta F_\alpha^X(\Delta \mathbf{r} \Delta \mathbf{p})_\alpha} = \bar{F}_\alpha^X(\Delta \mathbf{r} \Delta \mathbf{p})_\alpha \quad (30)$$

or, as  $(\Delta \mathbf{r}, \Delta \mathbf{p})_\alpha \rightarrow 0$ ,

$$\overline{\delta F_\alpha^X \delta F_\alpha^X} = \bar{F}_\alpha^X \delta(\mathbf{r}_\alpha - \mathbf{r}_{\alpha'}) \delta(\mathbf{p}_\alpha - \mathbf{p}_{\alpha'}) \quad (31)$$

in agreement with the identities (11) and (13).

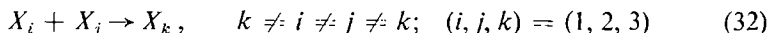
<sup>10</sup> At first sight, it is surprising to see that  $\zeta_\alpha$  is not proportional to the linearized collision term of eq. (15):  $-2 \sum_{jkl} A_{\alpha jkl} (\bar{F}_j^X \delta F_\alpha^X + F_\alpha^X \delta F_j^X)$ . This difference arises from the definition of the thermal fluctuations  $x_\alpha$  which are microscopic entities satisfying the property  $\int dx_\alpha x_\alpha P_1(x_\alpha, t) = 0$ . On the other hand, in the linearized Boltzmann equation,  $\delta F_\alpha^X$  is a *macroscopic* average. Notice that in a linear system or for a single degree of freedom, this difference disappears.

Integrating Eq. (3.1) over momenta and assuming that the velocity distribution remains Maxwellian, we recover a result similar to the generalized Einstein relation (2). Similarly, the distribution of the fluctuations [Eq. 28] is expressed in terms of the excess entropy [as Eq. (1)] and the correlations between fluctuations in different regions of position and velocity space vanish.

We see that in the *nonlinear, nonequilibrium* model discussed in this section, fluctuations behave in agreement with the generalized Einstein formula provided the system can be treated as a dilute mixture.<sup>11</sup> This substantiates the qualitative arguments advanced in the previous section. Comparing the two master equations (5) and (18) or the corresponding Fokker-Planck forms (7) and (25), one can easily see that the inadequacy of the usual birth-and-death formulation arises from an incorrect treatment of the internal states. For instance, Eqs. (5) and (7) imply that there is a finite probability that two molecules of  $X$  in the same state [cf. term containing  $P(X + 2)$  in Eq. (5) or factor four multiplying  $\partial x P / \partial x$  in Eq. (7)] switch simultaneously to another level. In other terms, Eq. (5) or (7) describes correctly a two-level system, but not a many-particle system such as a dilute reacting mixture, for which the probability of a simultaneous occupation of a level is vanishingly small in the thermodynamic limit  $\bar{X} \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $\bar{X}/V = \text{finite}$  [cf. conditions (16a)]. A bimolecular step or any other nonlinear process therefore introduces in the general phase-space master equation molecular occupations referring to *different* internal states. This distinction cannot be expressed consistently in the usual birth-and-death type of formulation.

Having developed the complete phase-space description, it is of some interest to investigate the possibility of obtaining a consistent *closed* equation in the number-of-particles space, which presumably will be different from Eq. (5) and will in general not describe a birth-and-death process.

Consider first the related problem in which a three-state assumption is made on model (3). In particular, one differentiates between active ( $X$ ) and inactive ( $A, M, E, D$ ) molecules and assumes that both types of molecules can occur in three different states. One also postulates the selection rule that only two  $X$ 's at different levels (1, 2, 3) may combine:



This set of steps replaces the second reaction in scheme (3). Assume now that the evolution of the three intermediates ( $X_1, X_2, X_3$ ) defines a birth-and-

<sup>11</sup> For dense mixtures or for systems far from local equilibrium, the results are no longer given by Einstein-type expressions. There is no reason to believe, however, that in this more complicated case, the usual birth-and-death type of master equation will again become adequate.

death process in the number-of-particles space. The master equation describing this process will have the same structure as the phase-space master equation (18) but the sums over  $(ij)$  or  $(kl)$  will contain only three terms corresponding to the pairs (12, 13, 23). Still, a given intermediate component index will occur twice in the sums. This property, together with factorization, is sufficient to ensure that fluctuations will behave exactly as in Eq. (29).

In conclusion, in a set of reactions involving  $n$  intermediates with stoichiometric coefficients  $r_i$  ( $i = 1, \dots, n$ ), one should allow for at least  $r_1 + \dots + r_n + 1$  independent variables (representing essentially different internal states) and impose factorization and the selection rule that in a reaction step, two particles cannot occupy the same state. Both rules are automatically satisfied in the thermodynamic limit as the number of levels tends to infinity [see Eqs. (16a) and (24)].

Let us now examine the possibility of deriving a closed master equation in the number-of-particles space. We define

$$P(X, t) = \sum_{\Sigma f_i^X = X} P(\{f_i^X\}, t) \quad (33)$$

In the generating function representation [cf. also Eq. (9)], this relation becomes

$$\begin{aligned} f(s, t) &= \sum_{\{f_i^X\} \geq 0} \prod_i s^{f_i^X} P(\{f_i^X\}, t) \\ &= \lim_{s_i = s} \mathcal{F}(\{s_i\}, t) \end{aligned} \quad (34)$$

$\mathcal{F}$  being the multivariable generating function of  $P(\{f_i^X\}, t)$ . Applying this transformation to the phase-space master equation (18), we obtain

$$\partial f / \partial t = k_1 A M (s - 1) f + \lim_{s_i = s} \sum_{ijkl} A_{ijkl} (1 - s_i s_j) (\partial^2 \mathcal{F} / \partial s_i \partial s_j) \quad (35)$$

We have defined<sup>(13)</sup>

$$k_1 = \sum_{ijkl} B_{ijkl} \bar{f}_i \bar{f}_j^M \quad (36)$$

We observe that the first term in the r.h.s. is identical to the corresponding term in Eq. (9a). This is due to the fact that in the master equation (18) the coefficient of the probability function  $P(f_k^X - 1, \{f'\}, t)$  is independent of the  $f^X$ 's. On the other hand, the second term of (35) is more complicated and in the general case is not reducible to a second derivative of  $f$  as in the corresponding term of Eq. (9a).

Suppose now one passes to the limit of an infinite system considered earlier in this section ( $X \rightarrow \infty, V \rightarrow \infty, X/V = \text{finite}$ ). Then, relation (33) becomes meaningless and the only correct description is in terms of the reduced distribution functions satisfying equations such as (22) or (25). Alternatively, in this case, the phase-space master equation cannot yield information about the structure of a master equation in  $X$ -space. Of course, once  $P_1(f_\alpha^X)$  is found and the factorization property (which implies an infinite system) is applied, one can construct  $P(X)$  from (33) as an *extrapolation* of a result which is really valid only in the limit  $X \rightarrow \infty$ .

Consider next the case of a finite system for which one can construct both  $P(X)$  and the master equation (35) in  $X$ -space. This time, in the phase-space master equation (18), the probability function  $P$  does not factorize and one can no longer derive a closed equation such as (25) for the reduced probabilities. In Eq. (35) this is translated by the fact that  $\mathcal{F}(\{s_i\})$  cannot be related in a simple way to  $f(s)$ . In fact, one can show that the condition resulting from identifying  $(\partial^2 \mathcal{F} / \partial s_i \partial s_j)_{\{s_i\}=s}$  with a derivative of  $f(s)$  implies an unphysical family of nonfactorizable generating functions  $\mathcal{F}(\{s_i\})$ . We may therefore conclude that in a finite system, the phase-space master equation cannot reduce to a closed equation for the probability function  $P(X)$ . Thus one should not expect the evolution of  $P(X)$  to be cast in the form of a birth-and-death type of master equation similar to (9a).

This conclusion is also supported by the results of the classical theory of fluctuations of concentration. The problem is formulated as follows. Consider a volume  $V$  containing  $N$  particles. What is the probability  $P(X, t)$  for finding at time  $t$ ,  $X$  particles in a small part  $\Delta V$  of the volume  $V$ ? The simplest possible case of independent colloidal particles each one of which performs Brownian motion has been analyzed in great detail by Kac.<sup>(14)</sup> He points out that in the limit  $N \rightarrow \infty, V \rightarrow \infty, N/V = \text{finite}$ , the process describing the number of particles in  $\Delta V$  at time  $t$  is *non-Markovian*. Still, the one time steady-state probability function  $P(X, t \rightarrow \infty)$  is a Poisson distribution.<sup>12</sup> We see that even in this simple case the birth-and-death process formulation is inadequate. *A fortiori*, this conclusion should remain valid for the chemical models considered in this section, in agreement with our previous remarks. Again, it does not seem possible to derive in this formalism a closed master equation for  $P(X, t)$ , owing to the very complicated dependence of this function on the probability distribution of the positions and velocities of the individual particles.

<sup>12</sup> We notice that the formulation in terms of a small volume  $\Delta V$  enables one to derive the distribution of  $X$  in a finite system from the properties of the infinite system ( $N, V$ ). The complications arising from the lack of factorization of  $P(\{f_i^X\})$  for a finite system are therefore avoided.

#### 4. THE VOLTERRA-LOTKA MODEL

In the preceding sections, we outlined the theory of nonequilibrium fluctuations for systems whose steady states are asymptotically stable. As a preliminary to the problem of fluctuations in the neighborhood of the onset of an instability, we consider in this section the Volterra–Lotka model which, as we shall see, lacks the property of asymptotic stability. Originally, this model was proposed for describing the competition between a number of predator–prey biological species.<sup>(16)</sup> More recently, it has been analyzed in great detail from a statistical mechanical point of view by Kerner<sup>(17)</sup> and Montroll *et al.*<sup>(18)</sup>

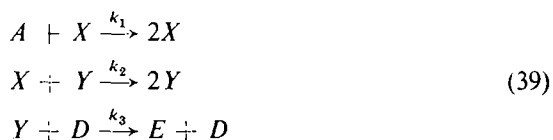
We shall be particularly interested in the case of two interacting species. The Volterra–Lotka equations describing this system read<sup>(16)</sup>

$$dX/dt = \epsilon_1 X - k_2 XY, \quad dY/dt = k_2 XY - \epsilon_3 Y \quad (37)$$

As usual,<sup>(16,17)</sup> we have assumed that the  $X$ – $Y$  coupling term appears with opposite sign in the two equations. Let us set

$$\epsilon_1 = k_1 A, \quad \epsilon_3 = k_3 D \quad (38)$$

It is easily seen that Eqs. (37) are then the conservation-of-mass equations of the following set of irreversible autocatalytic chemical reactions (in the limit of an ideal mixture):



As we shall see soon, this chemical analog of the Volterra–Lotka model will prove very useful for understanding the mechanism of fluctuations around instabilities.

Let us briefly recall the salient features of the evolution equations (37)<sup>(16,17)</sup>.

- (i) The system admits a single nonzero steady-state solution

$$X_0 = k_3 D / k_2, \quad Y_0 = k_1 A / k_2 \quad (40)$$

- (ii) Small perturbations around  $(X_0, Y_0)$  exhibit undamped oscillations with a universal frequency

$$\omega_0 = (k_1 k_3 A D)^{1/2} \quad (41)$$

- (iii) For arbitrary perturbations, Eqs. (37) admit a constant of motion

$$V(X, Y) = X + Y - (k_3 D / k_2) \ln X - (k_1 A / k_2) \ln Y \quad (42)$$



which defines for all  $X, Y > 0$  a set of closed curves. Thus, finite perturbations are also periodic in time with periods depending on the initial conditions. The trajectories corresponding to this motion are all orbitally stable (but *not* asymptotically stable).

We want now to study the behavior fluctuations around steady state (40) or around one of the periodic trajectories. To this end, it will first be assumed that Eqs. (37) define a Markovian birth-and-death process in the number-of-particles space. It is then easy to derive, as in Section 2, the equation of evolution for the reduced probability distribution  $P(X, Y, t)$  (summed over reservoir variables):

$$\begin{aligned}
 dP/dt = & A(X - 1) P(X - 1, Y, t) - AXP(X, Y, t) \\
 & + (X + 1)(Y - 1) P(X + 1, Y - 1, t) - XYP(X, Y, t) \\
 & + D(Y + 1) P(X, Y + 1, t) - DYP(X, Y, t)
 \end{aligned} \tag{43}$$

This equation has a very complicated structure and will only be analyzed here in the limit of small fluctuations around the steady state. Following the same procedure as in Section 2, one may reduce (43) to a Fokker-Planck-type equation of the form

$$\begin{aligned}
 \frac{\partial P(x, y, \tau)}{\partial \tau} = & \left( y \frac{d}{dx} - x \frac{d}{dy} \right) P(x, y, \tau) + \left[ \left( \frac{A}{D} \right)^{1/2} \frac{\partial^2 P(x, y, \tau)}{\partial x^2} \right. \\
 & \left. + \left( \frac{D}{A} \right)^{1/2} \frac{\partial^2 P(x, y, \tau)}{\partial y^2} - \frac{\partial^2 P(x, y, \tau)}{\partial x \partial y} \right]
 \end{aligned} \tag{44}$$

We have set

$$\begin{aligned}
 X = X_0 + D^{1/2}x, \quad Y = Y_0 + A^{1/2}y, \\
 k_1 = k_2 = k_3 = k, \quad \tau = (kAB)^{1/2}t
 \end{aligned} \tag{45}$$

It should be pointed out that the existence of an infinity of stable periodic trajectories in the Volterra-Lotka model implies that the Fokker-Planck limit should be taken with caution. In fact, the results derived from Eq. (44) can only describe *the short-time behavior around state* (40) when the fluctuations are expected to remain small.

From Eq. (44), one may derive a closed set of equations for the second moments of the probability distribution. Multiplying both sides by  $x^2, y^2, xy$ , integrating over  $x$  and  $y$ , and using the boundary conditions

$$P(\pm \infty, y) = P(x, \pm \infty) = 0 \tag{46}$$

one obtains

$$d\overline{x^2}/d\tau = -2\overline{xy} + 2\lambda, \quad d\overline{y^2}/d\tau = 2\overline{xy} + 2\lambda, \quad d(\overline{xy})/d\tau = \overline{x^2} - \overline{y^2} - 1 \tag{47}$$

with  $\lambda = (A/D)^{1/2}$ . It is immediately seen that this system *does not admit a steady-state solution*. The time-dependent solutions are easily constructed. The result is

$$\begin{aligned}\bar{x}^2 &= -\frac{1}{2}\{-\lambda + (1/\lambda)\} \sin 2\tau + \cos 2\tau\} + [\lambda + (1/\lambda)] \tau + \frac{1}{2} \\ \bar{y}^2 &= \frac{1}{2}\{-\lambda + (1/\lambda)\} \sin 2\tau + \cos 2\tau\} + [\lambda + (1/\lambda)] \tau + \frac{1}{2} \\ \overline{xy} &= \frac{1}{2}[-\lambda + (1/\lambda)](\cos 2\tau - 1) - \frac{1}{2} \sin 2\tau\end{aligned}\quad (48)$$

The initial conditions used are

$$(\overline{xy})_{\tau=0} = 0, \quad (\bar{x}^2)_{\tau=0} = (\bar{y}^2)_{\tau=0} = 1 \quad (49)$$

The last three conditions imply that initially the system behaved according to the generalized Einstein relations (1) and (2). We see that, in spite of this initial condition, the variances  $\bar{x}^2$  and  $\bar{y}^2$  increase in time, deviate immediately from the Poisson regime, and cannot reach a new steady state. Stochastically, therefore, the steady state (40) is meaningless, even in the limit of infinitesimal fluctuations. The system exhibits abnormal, critical fluctuations which increase linearly in time with a periodic "background noise." Ecologically this situation has a clear interpretation: The steady state prey distribution is never stable because there is no internal mechanism which reestablishes equilibrium once the latter is perturbed by the predator.

A closer study of the structure of the partial differential equation (44) helps to explain this peculiar behavior of the second moments. Indeed, Eq. (44) is elliptic everywhere in the  $(x, y)$  plane ( $-\infty < x, y < +\infty$ ). Qualitatively, therefore, it describes diffusion in an infinite medium without damping (because of the peculiar structure of the first derivative terms) and with an initial condition corresponding to a local inhomogeneity in the neighborhood of the origin. Thus, for  $\tau > 0$ , the system tends to "spread" in  $(x, y)$  space and smooth the initial inhomogeneity. Of course, for long times, new effects associated with large fluctuations are expected to modify this behavior.

## 5. PHASE-SPACE DESCRIPTION OF THE VOLTERRA-LOTKA MODEL

The results of the preceding section are direct consequences of the assumption that the Volterra-Lotka equations (37) define a Markovian process in  $(X, Y)$  space. On the other hand, the results of Section 3 prove that the chemical analog (39) of the ecological model requires a phase-space description of the kind discussed in the Section 3. In this description, it is implied that fluctuations define a Markovian process only in the complete phase space, including internal states. Assuming the system is maintained

uniform in space, it is easy to derive the two coupled Boltzmann equations for the average densities of particles of constituents  $X$  and  $Y$  in a given internal state (see Section 3 and Ref. 13):

$$d\bar{F}_\alpha^X/dt = - \sum_{jkl} A_{\alpha jkl} \bar{F}_\alpha^X \bar{F}_j^A + 2 \sum_{jkl} A_{jk\alpha l} \bar{F}_j^X \bar{F}_k^A - \sum_{jkl} B_{\alpha jkl} \bar{F}_\alpha^X \bar{F}_j^Y \quad (50a)$$

$$d\bar{F}_\beta^Y/dt = - \sum_{jkl} B_{\beta jkl} \bar{F}_j^X \bar{F}_\beta^Y + 2 \sum_{jkl} B_{jk\beta l} \bar{F}_j^X \bar{F}_k^Y - \sum_{jkl} C_{\beta jkl} \bar{F}_\beta^X \bar{F}_j^D \quad (50b)$$

The transition probabilities per unit time for reactive collisions  $A_{ijkl}$ ,  $B_{ijkl}$ ,  $C_{ijkl}$  satisfy conditions (16a) and the factors two have the same significance as in Eq. (15). Elastic collision terms have not been added, owing to the assumption that the system has attained a local equilibrium regime.

We observe that the structure of Eqs. (50a, b) is quite different from Eqs. (37) or their generalization to many components<sup>(16,17)</sup> in spite of the fact that on averaging (50a, b) over the internal states, one obtains (37) identically. The most striking difference is that in Eqs (37),  $dX/dt$  and  $dY/dt$  are proportional to  $X$  and  $Y$ , respectively. On the other hand, in Eqs. (50a,b),  $d\bar{F}_\alpha^X/dt$  is not proportional to  $\bar{F}_\alpha^X$  owing to the terms expressing, e.g., that two molecules of  $X$  in state  $\alpha$  may be created from  $X$  and  $Y$  in different internal states. Thus, one should not expect Eqs. (50a,b) to give rise to a constant of motion as in the Volterra or in the Kerner analysis.<sup>(16,17)</sup> Bearing also in mind the results derived in Section 3, one could anticipate that the phase-space description of fluctuations for the chemical Volterra-Lotka model (39) would be quite different from the picture outlined in the previous section.

Before we proceed to the analysis of fluctuations, we wish to emphasize that, independently of the chemical kinetic interpretation, the two levels of description given by Eqs. (37) and (50a,b) correspond to two largely different but interesting ecological situations. In the system described by Eqs. (37), it is assumed that the individuals forming the prey population are consumed by the predator without discrimination. When the predator population is comparable to or larger than that of the prey, it is reasonable to expect that this is indeed the most probable situation. However, in the more realistic case of small predator versus prey ratio, the most natural competition consumes preferentially those prey individuals having small values of some suitable "fitness" parameter which measures the ability to resist to or escape from the predator. It is then natural to expect that in such systems, in addition to the effect of predators, the internal processes determining the fitness distribution in the prey species<sup>13</sup> should play an important role. One of the

<sup>13</sup> As an example of such internal processes, one may cite the process of mutation in a bacterial population which may give rise to resistant mutants to, e.g., a viral attack or to a chemical substance.

consequences of these processes is to permit an *evolution* of the prey species in which the unfit individuals belonging to the tail of the internal distribution are eliminated continuously. Referring to the discussion at the end of Section 2, one can realize easily that this situation is well described by a set of equations of the type (50a,b), provided one suitably reinterprets the parameter  $\alpha$  determining the internal state.

Let us now study the fluctuations around the steady-state solution of Eqs. (50a,b). We assume that the latter define a Markovian process in the complete phase space. The corresponding master equation for the reduced probability distribution  $P(\{f^X\}, \{f^Y\}, t)$  reads

$$\begin{aligned}
 dP(\{f^X\}, \{f^Y\}, t)/dt &= \sum_{ijkl} A_{ijkl} \bar{f}_j^A [(f_i^X + 1) P(f_i^X + 1, f_k^X - 1, f_l^X - 1, \{f'\}, t) \\
 &\quad - f_i^X P(f_i^X, f_k^X, f_l^X, \{f'\}, t)] \\
 &\quad + \sum_{ijkl} B_{ijkl} [(f_i^X + 1)(f_j^Y + 1) \\
 &\quad \times P(f_i^X + 1, f_j^Y + 1, f_k^Y - 1, f_l^Y - 1, \{f'\}, t) \\
 &\quad - f_i^X f_j^Y P(f_i^X, f_j^Y, f_k^Y, f_l^Y, \{f'\}, t)] \\
 &\quad + \sum_{ijkl} C_{ijkl} \bar{f}_j^D [(f_i^Y + 1) P(f_i^Y + 1, \{f'\}, t) \\
 &\quad - f_i^Y P(f_i^Y, \{f'\}, t)]
 \end{aligned} \tag{51}$$

Again, we shall study this equation in the limit of small fluctuations. Using the same method as in Section 3 and imposing again the factorization condition (23) one obtains the following set of Fokker-Planck-type equations:

$$\begin{aligned}
 \frac{\partial P_1(x_\alpha, t)}{\partial t} &= \frac{\partial}{\partial x_\alpha} x_\alpha P_1(x_\alpha, t) \left[ 2 \frac{1}{\bar{f}_\alpha^X} \sum_{ijl} A_{ij\alpha l} \bar{f}_i^X \bar{f}_j^A - \frac{\partial(\ln \bar{f}_\alpha^X)}{\partial t} \right] \\
 &\quad + \frac{\partial^2 P_1(x_\alpha, t)}{\partial x_\alpha^2} \left[ 2 \sum_{ijl} A_{ij\alpha l} \bar{f}_i^X \bar{f}_j^A - \frac{1}{2} \frac{\partial \bar{f}_\alpha^X}{\partial t} \right]
 \end{aligned} \tag{52a}$$

$$\begin{aligned}
 \frac{\partial P_1(y_\beta, t)}{\partial t} &= \frac{\partial}{\partial y_\beta} y_\beta P_1(y_\beta, t) \left[ 2 \frac{1}{\bar{f}_\beta^Y} \sum_{ijl} B_{ij\beta l} \bar{f}_i^X \bar{f}_j^Y - \frac{\partial(\ln \bar{f}_\beta^Y)}{\partial t} \right] \\
 &\quad + \frac{\partial^2 P_1(y_\beta, t)}{\partial y_\beta^2} \left[ 2 \sum_{ijl} B_{ij\beta l} \bar{f}_i^X \bar{f}_j^Y - \frac{1}{2} \frac{\partial \bar{f}_\beta^Y}{\partial t} \right]
 \end{aligned} \tag{52b}$$

We have set

$$f_\alpha^X = \bar{f}_\alpha^X + x_\alpha, \quad f_\beta^Y = \bar{f}_\beta^Y + y_\beta \tag{53}$$

It should be pointed out that, strictly speaking, Eqs. (52) are *coupled* through the average values  $\bar{f}^X$  and  $\bar{f}^Y$  which have to satisfy the self-consistency conditions

$$\begin{aligned}\bar{f}_\alpha^X &::= \sum_{\{f^X\}, \{f^Y\}} f_\alpha^X P(\{f^X\}, \{f^Y\}, t) \\ \bar{f}_\beta^Y &= \sum_{\{f^X\}, \{f^Y\}} f_\beta^Y P(\{f^X\}, \{f^Y\}, t)\end{aligned}\quad (54)$$

This coupling, however, is quite different from that implied by Eq. (44), which does *not* admit factorizable solutions. To a first approximation (i.e., as long as one remains close to the reference state), one is allowed to identify the  $\bar{f}$ 's with the macroscopic averages appearing in the kinetic equations (50a,b). It follows that the friction coefficients in Eqs. (52) are always positive and therefore these equations *admit a steady-state solution which is stable with respect to small thermal fluctuations*. To calculate the probability distribution in this state, it is sufficient to set  $\partial P_1/\partial t = 0$ . Equations (52) reduce to a form similar to (27):

$$(\partial/\partial x_\alpha) x_\alpha P_1(x_\alpha) + \bar{f}_\alpha^X (\partial^2 P_1/\partial x_\alpha^2) = 0 \quad (55a)$$

$$(\partial/\partial y_\beta) y_\beta P_1(y_\beta) + \bar{f}_\beta^Y (\partial^2 P_1/\partial y_\beta^2) = 0 \quad (55b)$$

Again, the transition probabilities  $A_{ijkl}$  and  $B_{ijkl}$  cancel in these equations. The solution of (55a,b) is identical to (28) with

$$\overline{(\delta f_\alpha^X)^2} = \bar{f}_\alpha^X, \quad \overline{(\delta f_\beta^Y)^2} = \bar{f}_\beta^Y \quad (56)$$

We see that one recovers the generalized Einstein relations, as expected from the results of Section 3 and the qualitative arguments advanced in Section 2. Thus, the analysis based on the birth-and-death type of formulation of Section 4 is incompatible with the phase-space description outlined in this section. Comparing Eqs. (43) and (51) we see that the inadequacy of the former is due to the fact that, for instance, in the first step of the reaction scheme (39), it is implied that two molecules of  $X$  are produced in the same state as the molecule of  $X$  which combines with  $A$ . Now, in a macroscopic system in the thermodynamic limit, the probability of this event is negligible compared to the probability of the process described by the first term of Eq. (51). Hence, Eq. (39) cannot describe correctly the fluctuations in a thermodynamic system. Alternatively, a closed master equation in the number-of-particles space cannot describe a Markovian process.

The statistical properties of the Volterra–Lotka system have also been investigated by Kerner<sup>(17)</sup> and more recently by Montroll *et al.*<sup>(18)</sup> Kerner's

theory is based on the existence of a constant of motion [Eq. (42)] which is also shown to extend in the limit when the number of interacting species pairs goes to infinity. In this case, Kerner considers the kinetic equations (37) (suitably extended to an infinite number of variables) as *microscopic* equations of motion in a phase space spanned by

$$\begin{aligned} \text{coordinates} \quad u_{X_i} &= \ln(X_i/D_i) \\ \text{momenta} \quad u_{Y_i} &= \ln(Y_i/A_i) \end{aligned} \quad (57)$$

and derives a Liouville equation in the space of  $\{u\}$ 's. Combining this with an *additional*, equally *a priori* probability assumption, Kerner deduces an equilibrium solution of the form

$$P \propto \exp[-\beta V(\{X_i\}, \{Y_i\})] \quad (58)$$

Because of the additivity of  $V$  over species,<sup>(16,17)</sup>  $P$  is factorizable. Moreover, in the limit of small deviations from the steady state, it can be shown that<sup>(19)</sup>

$$V - V_0 \propto (\delta^2 S)_0 \quad (59)$$

where  $V_0$  is the value of  $V$  at the steady state. Thus,  $P$  reduces to the generalized Einstein distribution (1) and implies Eq. (2) for the mean quadratic fluctuations. In Montroll's analysis, a similar result is derived by adding fluctuating force terms in Eqs. (37) and assuming that for small deviations from the steady states, the correlation between these forces satisfies the same condition as in Brownian-motion theory.

We see that the results derived in this section are in qualitative agreement with the Kerner and Montroll theories in the limit of small fluctuations. The formulation and the domain of applicability of the two types of approaches are however quite different. In Eqs. (50)–(56), the index  $\alpha$  refers to internal states, whereas in Eq. (57),  $i$  refers to species number. Moreover, the kinetic equations (50a,b) which do not admit a constant of motion, are considered in our analysis as *macroscopic*, average equations of evolution and cannot themselves yield information about fluctuations. The latter are not introduced artificially in the problem but are direct consequences of the dynamics of a many-body system in phase space.<sup>(11,14)</sup>

In Kerner's analysis, the information about fluctuations does not come from the original Volterra-Lotka equations but rather from the additional equally *a priori* probability assumption. In principle, the reasonableness of this assumption cannot be controlled. In the limit of small deviations from the steady state, the results of this section prove, implicitly, that it becomes justified.

## 6. DISCUSSION

In this paper, we have shown that in nonlinear open systems undergoing chemical reactions far from thermodynamic equilibrium, it is necessary to adopt a stochastic description based on the Boltzmann equation in order to describe correctly the distribution of thermal fluctuations around steady states. It is only in the limit when the state of the system is close to equilibrium and also in the case of unimolecular reactions (linear systems) that this more complete description does not contradict the results based on the usual birth-and-death process formulation. As a consequence of this result, in dilute mixtures, small thermal fluctuations behave according to a generalization of the Einstein relations, even when the reference state of the system is not asymptotically stable (as in Sections 4 and 5).

We believe that the conclusions reached in Section 5 provide a valuable insight to the problem of the onset of oscillations and instabilities in macroscopic physics. Indeed, a system in the neighborhood of an instability behaves in much the same way as the Volterra–Lotka model in the sense that macroscopically, small perturbations are not damped or amplified. Now, the analysis of Section 5 shows that in the phase-space description, *small thermal fluctuations are damped*. At first sight, this result may seem paradoxical. Because of the infinity of periodic trajectories around the steady state in the Volterra–Lotka model, one would expect that the system may have no criteria to choose the “right” or most probable regime and that this inability would manifest itself by abnormal fluctuations of some kind, which is ruled out by the results of Section 5. How, then, can a system at or slightly beyond a state of marginal stability be driven to the new regime beyond instability by thermal fluctuations? We believe that the answer to this question may be as follows.

(i) First, it has to be realized that the lack of asymptotic stability or the instabilities observed in nonlinear dissipative systems (chemical instabilities, turbulence, etc.) are purely macroscopic phenomena which have no direct molecular analogs as long as the system is maintained in a local equilibrium regime. It is therefore reasonable to expect that systems undergoing such *macroscopic instabilities* cannot evolve from a given macroscopic reference state by a mechanism of thermal fluctuations of usual size (i.e., very small). This explains why small fluctuations are damped in the Boltzmann equation description for the model discussed in Section 4 and 5. Instabilities such as plasma instabilities<sup>(20)</sup> or laser thresholds<sup>(21)</sup> are, on the other hand, *instabilities in the velocity distribution* and cannot be described in the framework of a local equilibrium theory. While such “molecular” instabilities can be thought of as second-order phase transitions,<sup>(21)</sup> macroscopic instabilities appear to be more closely related to first-order phase transitions.

(ii) A change in the macroscopic state of a system in a local equilibrium regime has therefore to arise from a mechanism of *large thermal fluctuations* of macroscopic size. Again, this substantiates the analogy with a first-order phase transition. The probability of these fluctuations is very small. As a result, even during the macroscopic evolution, the generalized Einstein relation (2) would be practically satisfied around the *true* (time-dependent) average. The time required for the formation of this evolving mode would thus be necessarily macroscopic, i.e., very long compared to the relaxation time between molecular collisions. In fact, it should be comparable to the “hydrodynamic” scale of macroscopic evolution.

(iii) The probability that such a finite fluctuation occurs everywhere in a macroscopic system should be practically vanishing. Rather, the most natural molecular mechanism underlying a macroscopic evolution should be as follows. A small subsystem (containing, say  $10^2$  particles) begins to evolve as a result of a finite fluctuation. This creates a local inhomogeneity which in usual circumstances would tend to be damped by diffusion. However, if the system is near the threshold of a macroscopic transition, diffusion should rather provide a mechanism for propagation over macroscopic distances of the disturbance created by a fluctuation.

In order to substantiate these conjectures, it would be necessary to solve the master equation (51) in a way which takes into account, self-consistently, the simultaneous evolution of fluctuations of all possible sizes *and* of the macroscopic state. This means that one has to study the time-dependent solutions of Eq. (51) including the effect of arbitrarily large fluctuations<sup>14</sup> and imposing for any macroscopic state the self-consistently condition (54). This study, which should provide such information as, e.g., the critical size of fluctuations beyond which the system starts evolving, is presently in progress.

As we briefly discussed in Section 4 and 5, the critical behavior of fluctuations predicted by the birth-and-death type of analysis of Section 4 is not expected to occur in a local equilibrium regime but rather is peculiar to certain types of ecological models. It is interesting to compare this conclusion with a recent result by Mazo,<sup>(22)</sup> who also finds a critical fluctuation behavior in the neighborhood of an instability of the macroscopic equations of evolution. Essentially, Mazo shows that in this limit, the friction coefficient which would appear in a Fokker–Planck equation in the numbers-of-particles space vanishes and therefore the mean quadratic fluctuations start growing in time. This is quite similar to the behavior described by Eqs. (48) of this paper. Again, in a realistic chemical kinetic system, this type of evolution should only be expected to describe large fluctuations of macroscopic size. Small

<sup>14</sup> In this case, the probability distribution is expected to be different both from the generalized Einstein form and from the distribution derived by Kerner.



thermal fluctuations should still be damped as in the model discussed in Section 5.

Independently of their possible interest for the understanding of instabilities, the results of this paper have some implications in the field of nonlinear thermodynamics of irreversible processes. Consider a dilute system of  $X$  particles in a local equilibrium regime ( $X$  may refer to a chemical constituent of a reacting mixture). According to kinetic theory, the state of the system  $\rho$  is completely determined by the singlet distribution function  $\bar{F}_1$  (in the notation of Section 2 to 5):

$$\rho(1, \dots, X) = Ct \prod_{i=1}^X \bar{F}_1(i) \quad (60)$$

:  $O(\text{deviations from local equilibrium})$

where

$$\int dx \bar{F}_1(i) = \bar{X} \quad (61)$$

$\alpha$  being an index comprising all variables but the number of particles (e.g., momenta). A straightforward consequence of (60) and (61) is that the distribution of  $X$  is given by the Poisson law<sup>(23)</sup>:

$$P(X) = (1/X!) \int \{dx_i\} \rho = (\exp -\bar{X})(\bar{X}^X/X!) \quad (62)$$

which reduces in the limit of small fluctuations to the Einstein formula (1), whether  $\bar{X}$  stands for an equilibrium or for a steady-state average.

Consider now the entropy of the system in the grand canonical ensemble. Again, because of local equilibrium, we expect

$$S = -k \sum_{X=0}^{\infty} \int \{dx_i\} \rho \log \rho \quad (63)$$

$$= -k\bar{X} \sum_{X=0}^{\infty} P[\log(\bar{X}/V) - \bar{X} + X \log \bar{X} - \log X!] + S_0(\bar{X})$$

where  $S_0(\bar{X})$  contains terms related to internal energy. Applying Stirling's formula and expanding  $S$  to second-order terms, one finds

$$S = -k\bar{X} \log(\bar{X}/V) + S_0(\bar{X}) + \frac{1}{2} \overline{\delta^2 S} \quad (64)$$

where

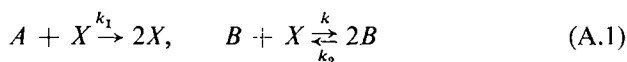
$$\frac{1}{2} \overline{\delta^2 S} = -\bar{X} [(\overline{\delta X})^2 / 2\bar{X}^2] \quad (65)$$

is the value of the second-order excess entropy around the steady state as predicted by local equilibrium thermodynamics.

We see that the validity of the Poisson law and the local equilibrium assumption permit us to extend the formalism of statistical mechanics and thermodynamics to include fluctuations, in the sense that the probability distribution of the latter determines uniquely the entropy of fluctuations. This is in agreement with the Glansdorff-Prigogine approach to the nonlinear thermodynamics of irreversible processes.<sup>(1)</sup>

## APPENDIX: FLUCTUATIONS IN AN AUTOCATALYTIC SYSTEM

Consider the autocatalytic scheme



which is similar to one of the models treated by Hawkins and Rice.<sup>(5)</sup>

The inverse reaction in the first step is neglected. The system is open to  $A$  and  $B$  and for simplicity we set  $k_1 = k_2 = 1$ . The equation of mass conservation reads

$$dX/dt = (A - kB)X + B^2 \quad (\text{A.2})$$

with the steady-state solution

$$X_0 = B/[k - (A/B)] \quad (\text{A.3})$$

In contrast to (4a), this equation is linear in  $X$ . However, system (A.1) is intrinsically nonlinear and will now be shown to exhibit non-Poisson fluctuations.

The reduced master equation in the number-of-particles space of component  $X$  reads

$$\begin{aligned} dP(X, t)/dt = & A(X - 1)P(X - 1, t) - AXP(X, t) \\ & + kB(X + 1)P(X + 1, t) - kBXP(X, t) \\ & + B^2P(X - 1, t) - B^2P(X, t) \end{aligned} \quad (\text{A.4})$$

In the generating function representation [cf. (9)], Eq. (A.4) transforms to

$$\partial f / \partial t = [A(s^2 - s) + kB(1 - s)](\partial f / \partial s) + (s - 1)B^2f \quad (\text{A.5})$$

In the steady state, one obtains

$$[k - (A/B)s](\partial f / \partial s) - Bf = 0 \quad (\text{A.6})$$

The properly normalized solution of this equation is

$$f = [k - (A/B)]^{B^2/A} [k - (A/B)s]^{-B^2/A} \quad (\text{A.7})$$

Computing the moments of  $P$  from (A.7), one finds

$$\bar{X} = (\partial f / \partial s)_{s=1} = B/[k - (A/B)] = X_0 \tag{A.8}$$

$$\overline{\delta X^2} = (\partial^2 f / \partial s^2)_{s=1} - (\partial f / \partial s)_{s=1}^2 + (\partial f / \partial s)_{s=1} = X_0(1 + \mu) \tag{A.9}$$

with

$$\mu = (A/B)/[k - (A/B)] \tag{A.10}$$

We see that we obtain, as in Section 2, a distribution function which is different from the Poisson or the generalized Einstein results (1)–(2). The deviation from (2) is proportional to the factor  $\mu$  defined in Eq. (A.10) and is seen to depend on the explicit properties of the two steps in (A.1). It is only in the limit as  $k \rightarrow \infty$  or  $A/B \rightarrow 0$  that one recovers a Poisson-type variance. The analysis of Section 2 is thus confirmed: If the equations of mass conservation of a nonlinear, nonequilibrium system are assumed to define a birth-and-death process in the number-of-particles space, one obtains a steady-state distribution of fluctuations which is different from the generalized Einstein formula.

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