

# A Master Equation Description of Local Fluctuations

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A theory of fluctuations of macrovariables in nonequilibrium systems based on a nonlinear master equation is outlined. This equation takes into account, via a "mean field" type of approximation, the effect of the spatial extension of fluctuations. A comparison with the birth and death formalism reveals several unsatisfactory features of the latter.

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**KEY WORDS:** Fluctuations; stochastic processes; master equations; nonlinear systems; nonequilibrium thermodynamics.

## 1. INTRODUCTION

The importance of fluctuations in the behavior of complex systems is well recognized. Such phenomena as equilibrium phase transitions,<sup>(1)</sup> hydrodynamic instabilities,<sup>(2)</sup> the onset of dissipative structures in nonlinear reaction diffusion systems far from equilibrium,<sup>(3,4)</sup> or the extinction of a species in a system of interacting populations<sup>(5)</sup> are all due primarily to fluctuations. The latter modify qualitatively the macroscopic regime described by the conservation equations and confer to the evolution an essentially statistical character.

In this paper we are concerned with the description of fluctuations in *nonlinear, nonequilibrium* systems undergoing chemical reactions and diffusion. Most of our results will refer to macroscopically homogeneous systems described by the familiar mass conservation equations:

$$dN_i/dt = \sum_p v_{ip} w_p(\{N_j\}) \equiv f_i(\{N_j\}), \quad i = 1, \dots, n \quad (1)$$

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$\nu_{i\rho}$  are the stoichiometric coefficients and  $w_\rho$  the velocity of reaction  $\rho$ . The  $N_i$  are composition variables (densities, mole fractions, or even particle numbers). From time to time we shall present some generalized results applicable to inhomogeneous systems as well:

$$\partial N_i / \partial t = f_i(\{N_j\}) + D_i \nabla^2 N_i, \quad i = 1, \dots, n \quad (2)$$

where  $\{D_i\}$  are the diffusion coefficients of the chemical species. It is well known that the solutions of systems (1) and (2) present several unexpected features, such as limit cycle behavior, spatial ordering, or wavelike activity.<sup>(6)</sup> Following Prigogine, we shall call these regimes *dissipative structures*.

Traditionally, fluctuations in chemical systems have been studied by means of the so-called master equations of the birth and death type.<sup>(7)</sup> This formalism was extended to nonequilibrium situations by Babloyantz, Prigogine, and Nicolis.<sup>(3,4,8,9)</sup> The following results have been established.

(a) At equilibrium the probability distribution in an ideal reacting mixture under open system conditions is a Poisson distribution and reduces to the Einstein law in the limit of a large number of particles.

(b) Result (a) extends to linear systems (unimolecular reactions) arbitrarily far from equilibrium.

(c) Nonlinear systems behave in a distinctly non-Poisson fashion. In particular, the mean square deviation of fluctuations becomes

$$\langle \delta X^2 \rangle = \langle X \rangle (1 + \mu) \quad (3)$$

where the factor  $\mu$  is system dependent. In systems lacking asymptotic stability,  $\mu$  diverges or depends explicitly on time.<sup>(3)</sup>

On the basis of these conclusions, Prigogine and Nicolis challenged the validity of the birth and death formalism and observed that the highly non-Poisson behavior is incompatible with the fact that, on the average, the systems described are quite close to local equilibrium. Subsequently, they developed a completely local *phase space* description of fluctuations<sup>(3,10,11)</sup> which predicted a Poisson behavior for *small* thermal fluctuations. Large-scale fluctuations appear, on the other hand, to be correctly described by a birth and death type formalism. These results suggest<sup>(3,4,10,11)</sup> that the amplification of fluctuations leading to an instability involves a mechanism of *nucleation* of fluctuations in a suitable subvolume, and that beyond a critical size of the nucleus the fluctuations will spread and "contaminate" the entire system.

Quite recently there has been a considerable controversy on the status of both the birth-and-death and the phase-space descriptions. Thus Saito<sup>(12)</sup> claimed that the birth and death formalism always gives a Poisson-like covariance for the fluctuations in the limit of large systems. Kuramoto<sup>(13)</sup> and Nitzan and Ross<sup>(14)</sup> suggested the seemingly opposite result: Namely, that

the phase-space description predicts in general non-Poisson behavior. Replies to the comments of these authors have been given recently by Nicolis *et al.*<sup>(11)</sup> and by Mazo.<sup>(15)</sup>

The purpose of the present paper is to reexamine the foundations of the birth and death formalism and to develop a simplified theory of local fluctuations in nonequilibrium systems. In Section 2 we examine the equilibrium limit of the birth and death master equations. We show that the validity of the Poisson distribution in this limit implies a *unique* form of the transition probabilities appearing in this formalism. In Section 3 we point out a number of deficiencies of this formalism with the form of transition probabilities derived in Section 2. Section 4 is devoted to an extension of the birth and death theory permitting a description of local fluctuations. Our analysis,<sup>2</sup> which appears to be “intermediate” between the birth-and-death and phase-space approaches, has the principal virtue of simplicity as opposed to the rather complicated phase-space master equations. The properties of the master equation are analyzed in Sections 5 and 6. The applications of the formalism to the analysis of instabilities are reported in a forthcoming paper by Van Nypelseer, Kitahara, and the authors.

## 2. THE EQUILIBRIUM LIMIT

In this section, as well as in Section 3, we shall adopt the usual assumption that Eq. (1) defines a *Markov process* of the birth and death type *in the space of the numbers of particles* of the various constituents. The evolution of the probability distribution  $P(\{X_l\}, t)$  for having, at time  $t$ ,  $X_l$  particles of constituent  $l$  ( $l = 1, \dots, n$ ) is given by a Kolmogorov-type equation:

$$\begin{aligned} dP(\{X_l\}, t)/dt = & \sum_{\rho} W(\{X_l - \nu_{l\rho}\} \rightarrow \{X_l\})P(\{X_l - \nu_{l\rho}\}, t) \\ & - \sum_{\rho} W(\{X_l\} \rightarrow \{X_l + \nu_{l\rho}\})P(\{X_l\}, t) \end{aligned} \quad (4)$$

subject to

$$P \geq 0; \quad \sum_{\{X_l\}} P(\{X_l\}, t) = 1, \quad \forall t; \quad \sum_j W(i \rightarrow j) = 0 \quad (5)$$

$r_{l\rho}$  is the step of variation of  $X_l$  in the  $\rho$ th reaction. The first problem that arises in connection with the birth and death formalism is to determine the transition probabilities per unit time  $W$  in an unambiguous fashion. We shall first assume that  $W$  is independent of  $P$ . Although it is generally agreed that  $W$  should then be a polynomial in  $X_l$ 's, a general form of this polynomial has not been adopted universally. Thus the expression

$$W(X + r \rightarrow X) \propto (X + 1) \cdots (X + r) \quad (6)$$

<sup>2</sup> Preliminary accounts of this description are found in Refs. 4, 16, and 17. Similar approaches have been adopted recently by Kuramoto<sup>(16)</sup> and by Nitzan *et al.*<sup>(19)</sup>

based on combinatorial arguments is frequently replaced by expressions such as

$$W(X + r \rightarrow X) \propto (X + 1)^r, \quad \text{etc.} \quad (7)$$

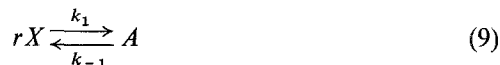
We shall now show that if, in addition to (5) we impose the condition that, in an *ideal* mixture at equilibrium:

$$P_{\text{equil}} = P_{\text{Poisson}} = e^{-\langle X \rangle} \langle X \rangle^X / X! \quad (8)$$

then  $W$  is determined uniquely. We may note that (8) is a *rigorous* consequence of the statistical mechanics of ideal systems.<sup>(1)</sup> Moreover it does *not* involve any asymptotic approximation on  $X$  or  $\langle X \rangle$ , but only on the size of the entire system (chemicals + solvent), which is taken to be large.

### 2.1. A Simple Example

We consider the following reactions (in an open system):



$A$  is considered to be in excess and will therefore be treated as a constant. This decoupling assumption, discussed in Ref. 8, need *not* involve any asymptotic approximation on  $X$  but relies entirely on the limit  $A \rightarrow \infty$ . At the steady state, Eq. (4) becomes

$$0 = W(X + r \rightarrow X)P(X + r) - W(X \rightarrow X - r)P(X) + k_{-1}AP(X - r) - k_{-1}AP(X), \quad 0 \leq X \leq \infty \quad (10)$$

Note that the transition probability for the back reaction has been written as  $k_{-1}A$ ,<sup>(8)</sup> due to the linear character of this step.

From Eq. (10) it follows that

$$f(X) \equiv W(X + r \rightarrow X)P(X + r) - k_{-1}AP(X) = f(X - r), \quad \forall X \quad (11)$$

The only nonoscillatory solution of (11) is

$$f(X) = \text{const} = C = 0 \quad (12)$$

Indeed, from (11) it follows that  $C = f(X - r)$ , which vanishes identically for  $X < r$ . Thus

$$W(X + r \rightarrow X) = k_{-1}AP(X)/P(X + r)$$

or, from (8) at equilibrium,

$$W(X + r \rightarrow X) = k_{-1}A \langle X \rangle^{-r} (X + 1) \cdots (X + r) \quad (13)$$

Insofar as  $W$  is independent of  $P$ —and thus also of  $\langle X \rangle$ —Eq. (13) imposes

$$k_{-1}A = \lambda \langle X \rangle^r \quad (14)$$

$$W(X + r \rightarrow X) = \lambda (X + 1) \cdots (X + r) \quad (15)$$

where  $\lambda$  is a *numerical* constant. The point is that (14) is identical to the law of mass action, provided

$$\lambda = k_1/r! \tag{16}$$

It follows that

$$W(X + r \rightarrow X) = k_1(X + 1) \cdots (x + r)/r! \tag{17}$$

in agreement with (6). Note that  $k_{-1}$  and  $k_1$  are, respectively, of the order of (volume)<sup>-1</sup> and (volume)<sup>-r</sup>. The open system assumption  $X/A \ll 1$  can be ensured with  $k_{-1}/k_1 \ll 1$ .

A remarkable corollary of this result is that equilibrium chemical kinetics [Eq. (14)] appears to be an *exact* consequence of the master equation and of the Poisson distribution, in the sense that it does not seem to involve any asymptotic assumption on the size of  $\langle X \rangle$ . Stated differently, in a fluctuating system, the Guldberg–Waage law keeps exactly the form (14) rather than the form

$$k_1 A = \lambda \langle X^r \rangle \tag{18}$$

Some brief remarks in the same direction can be traced back to Landau and Lifshitz.<sup>(1)</sup>

### 2.2. The General Case

We now consider an arbitrary step in an equilibrium chain, e.g.,



The contribution of this step to the master equation reads

$$\begin{aligned} dP(X, \{X'\})/dt = & W(X + r \rightarrow X; \{X'\})P(X + r, \{X'\}) \\ & - W(X \rightarrow X - r; \{X'\})P(X, \{X'\}) + \dots \end{aligned} \tag{20}$$

In the case of a Poisson distribution we want (20) to reduce to the macroscopic kinetic laws exactly, or, more precisely, up to terms of  $O(1/E, \dots)$ , where  $\{E, \dots\}$  are the reservoir variables kept constant. Taking the average of (20) after multiplying with  $X$ , one obtains

$$\begin{aligned} \lim_{P(X) \rightarrow \text{Poisson}} \sum_{X=0}^{\infty} [XW(X + r \rightarrow X)P(X + r) \\ - XW(X \rightarrow X - r)P(X, t)] = -rk \frac{\langle X \rangle^r}{r!} \end{aligned} \tag{21}$$

where [cf. (19)]

$$k = k_1\{\dots\}$$

Adding and subtracting  $r$  from  $X$  in (21), one finally obtains the following condition on  $W$ .

$$\lim_{P(X) \rightarrow \text{Poisson}} \sum_{X=0}^{\infty} W(X+r \rightarrow X)P(X+r) = k\langle X \rangle^r/r! \quad (22)$$

We know that Eq. (22) admits at least one solution, namely the function  $W \equiv W_0$  given by Eq. (17). To show the uniqueness of  $W_0$  in the general case it will be sufficient to show that the equation

$$\sum_{X=0}^{\infty} [W(X+r \rightarrow X) - W_0]P^{\text{Poisson}}(X+r) = 0 \quad (23)$$

admits only the trivial solution, provided  $W$  and  $W_0$  are not functions of  $P$  or of its moments. By differentiating (23) successively with respect to  $\langle X \rangle$  appearing in the Poisson distribution [cf. Eq. (8)], one can show straightforwardly that this equation engenders an infinity of relations of the form

$$\sum_{X=0}^{\infty} X^N [W - W_0]P(X) = 0, \quad \forall N \quad (24)$$

Thus  $(W - W_0)P(X)$  vanishes identically, being orthogonal to all polynomials. Since  $P(X)$  is positive, this implies

$$W \equiv W_0 \quad (25)$$

The uniqueness theorem is thus proven.

### 3. CRITIQUE OF THE BIRTH AND DEATH FORMALISM

Having now an explicit and unambiguous form for the birth and death transition probabilities, we shall proceed to a critical analysis of this formalism when applied to *nonequilibrium* situations.

It is not difficult to advance a great number of intuitive arguments pointing out several deficiencies of the birth and death formulation. In the first place, the fact that the transition probabilities are computed in terms of "collective" variables referring to the entire system [see Eq. (17)] should overestimate these quantities. In a chemical mixture only those particles that are sufficiently close will be able to undergo a reactive collision. Equally crucial is the fact that the description of fluctuations is global in the sense that the system is treated as if it remained homogeneous. This discards such properties as the *size* and the intrinsic *range*, or *coherence length*, of the fluctuations. One expects that these properties should play an important role in the *onset* of cooperative behavior beyond an instability leading to a dissipative structure.

We shall now show, on an explicit example, that the birth and death formalism can become quite inadequate and give rise to results which are

opposite to the predictions based on macroscopic analysis. We consider the model



The system is open to  $A$  and  $E$  and is assumed to remain homogeneous. Moreover, due to the irreversible character of the reactions, it operates under highly nonequilibrium conditions. The macroscopic equations of mass balance are

$$d\bar{X}/dt = k_1A\bar{X} - k_2\bar{X}^2 \tag{27}$$

where  $\bar{X}$  is the composition variable of species  $X$ . It is easily seen that (27) admits two steady state solutions. The trivial one

$$\bar{X}_0 = 0 \tag{28a}$$

which is *unstable*, and the solution

$$\bar{X}_0 = k_1A/k_2 \tag{28b}$$

which is *asymptotically stable* with respect to all perturbations.

The master equation becomes [see Eqs. (4) and (17)]

$$\begin{aligned} dP(X, t)/dt &= k_1A(X - 1)P(X - 1, t) - k_1AXP(X, t) \\ &+ k_2 \frac{(X + 1)(X + 2)}{2} P(X + 2, t) \\ &- k_2 \frac{X(X - 1)}{2} P(X, t) \end{aligned} \tag{29}$$

The steady state solution  $P_0$  of this equation is defined by the set

$$dP_0(0)/dt = k_2P_0(2) = 0 \tag{30a}$$

$$dP_0(1)/dt = -k_1AP_0(1) + 3k_2P_0(3) = 0 \tag{30b}$$

$$\begin{aligned} dP_0(2)/dt &= k_1AP_0(1) - 2k_1AP_0(2) + 6k_2P_0(4) - k_2P_0(2) = 0 \\ &\vdots \end{aligned} \tag{30c}$$

From (30a) and (30c) as well as from  $P(k) \geq 0$  it follows that

$$P_0(1) = P_0(4) = P_0(2) = 0 \tag{31}$$

and from (30b) and (31)

$$P_0(3) = 0 \tag{32}$$

This result extends to all  $P_0(k)$  for  $k > 4$ . Thus, the steady state solution of (29) is

$$P_0(k) = \delta_{k,0}^{kr} \tag{33}$$

Due to the linearity of the master equation this solution will be unique. The surprising aspect of this result is that the birth and death formalism seems to have destroyed the stable solution of the macroscopic equation (27) and preserved, instead, the physically unacceptable trivial (and unstable) solution: Even if the system starts initially with a great number of  $X$  particles, it will be driven eventually to extinction. Yet the master equation for the *same* system near equilibrium admits the Poisson distribution as a unique steady state solution!

The conclusion to be drawn from this analysis can only be that the birth and death transition probabilities are not written correctly. Now, according to Section 2, these probabilities are unique as long as they do not depend on the probability distribution or on its moments.

A first way to overcome the difficulties of the formalism would be, therefore, to introduce transition probabilities which are functionals of  $P$ . Unfortunately, there is no obvious method of evaluating these probabilities from first principles.

A more satisfactory solution is suggested by our remarks at the beginning of this section about the overestimating of the transition probabilities in a large system. A natural remedy of this would be to apply the birth and death analysis to a subvolume  $\Delta V$  of the entire system, which is sufficiently small that all the particles included there have an appreciable probability of undergoing a reactive collision during a time interval short with respect to the scale of the macroscopic evolution. One can expect reasonably that within  $\Delta V$  the stochastic process generated by Eq. (1) would become Markovian, provided one can also account for the coupling between  $\Delta V$  and the remainder of the system. This coupling arises through the transport of matter and energy across the surface separating  $\Delta V$  and  $V - \Delta V$ . In the following section we shall derive a master equation enabling such a *local* description of fluctuations, which does not share the pathological features of the birth and death formalism.

It is remarkable that near equilibrium the necessity of a local description of fluctuations is not apparent. In a sense, near equilibrium the entire system or different small parts of it behave in an identical fashion and are both described by a Poisson distribution. As soon as the system deviates from equilibrium, the constraints introduce coupling between neighboring spatial elements as well as between the chemical steps. As a result, a global description of fluctuations of the birth and death type becomes inadequate.

#### 4. NONLINEAR MASTER EQUATION

We consider an ideal chemical mixture and a small part  $\Delta V$  of the overall reaction volume  $V$  surrounded by the surface element  $\Delta \Sigma$ .  $\mathbf{n}$  is the outward



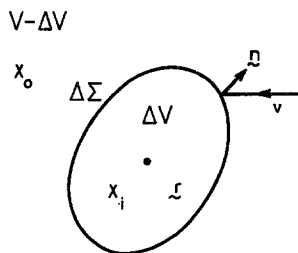


Fig. 1

normal to  $\Delta\Sigma$  (Fig. 1). We assume that the system remains macroscopically homogeneous, although the density and composition fluctuations continuously *break* this homogeneity locally, within small subvolumes like  $\Delta V$ .

In order to preserve simplicity, we shall adopt a local but *discrete* description of fluctuations. In other terms, the values of the composition variables at each point in space will be redefined as<sup>(2)</sup>

$$\rho_{x_i}(\mathbf{r}) \equiv \rho_{x_i}(\Delta V) = X_i/\Delta V \tag{34}$$

whereas

$$\langle \rho_{x_i} \rangle_{\Delta V} = \left[ \sum_{X_i=0}^{\infty} X_i P(X_i, \Delta V, t) \right] / \Delta V \tag{35}$$

Here  $X_i$  denotes the numbers of particles of a set of chemical components within  $\Delta V$ . A summation over the various components is implied in (35) and throughout this section. Naturally, relations (34) and (35) remain meaningful provided the volume  $\Delta V$  surrounding  $\mathbf{r}$  is sufficiently small. Subsequently, the size of  $\Delta V$  will be related to the *range* of a local fluctuation. As the latter remain small in their overwhelming majority, we expect this condition on  $\Delta V$  to be satisfied.

The fluctuations of composition within  $\Delta V$  will be given by

$$\delta \rho_{x_i}(\Delta V) = (X_i/\Delta V) - \langle \rho_{x_i} \rangle_{\Delta V} \tag{36}$$

We expect that

$$\lim_{\Delta V \rightarrow 0} \langle \rho_{x_i} \rangle_{\Delta V} = \text{finite} \tag{37}$$

and equal to the local value of the density of  $X$  at the point  $\mathbf{r}$ . In contrast to this,  $\delta \rho_{x_i}$  need not be a smooth function of  $\Delta V$ . True,  $\delta \rho_{x_i}$  can become as small as may be desired if  $\Delta V$  is sufficiently large. However, if  $\Delta V$  is small,  $\delta \rho_{x_i}$  can become comparable to or even greater than  $\langle \rho_{x_i} \rangle$ . Thus, the sub-volume  $\Delta V$  considered in this section will in fact be associated with the intrinsic properties of the fluctuations.

Let  $P(X_i, X_o, t)$  be the probability distribution of the entire system, where  $X_o$  is the number of particles of the constituents outside  $\Delta V$ . We denote  $R_{ch}$  the contribution of the chemical reactions to the evolution of  $P$ . Due to

their local character, the latter will give additive contributions to this evolution if the mixture is ideal. Thus

$$dP(X_i, X_0, t)/dt = R_{ch}(\Delta V) + R_{ch}(V - \Delta V) + T(\Delta V, V - \Delta V) \quad (38)$$

where  $T$  is a term coupling  $\Delta V$  to the surroundings through the transport of matter and energy. In this section we shall be concerned exclusively with the transport of matter. Thus, we assume that we deal with a mixture of very large thermal conductivity. The extension of our results to the nonisothermal case has been carried out recently by Franckson.<sup>(20)</sup> The interaction term reduces to

$$\begin{aligned} T = & W_{out}(X_i - 1 \rightarrow X_i; X_0 + 1 \rightarrow X_0)P(X_i - 1, X_0 + 1, t) \\ & + W_{in}(X_i + 1 \rightarrow X_i; X_0 - 1 \rightarrow X_0)P(X_i + 1, X_0 - 1, t) \\ & - [W_{out}(X_i; X_0) + W_{in}(X_i; X_0)]P(X_i, X_0, t) \end{aligned} \quad (39)$$

The transition probabilities per unit time  $W_{out}$  and  $W_{in}$  describe the frequency of passage of  $X$  particles across  $\Delta\Sigma$ . Let  $f_0(\mathbf{r}, \mathbf{v}, t)$  and  $f_i(\mathbf{r}, \mathbf{v}, t)$  be the probability density distributions of position and momenta for component  $X$ . According to kinetic theory of gases,<sup>(21)</sup>

$$W_{out} = -\oint_{\Delta\Sigma} dS \int d\mathbf{v} \mathbf{v} \cdot \mathbf{n} \theta(-\mathbf{v} \cdot \mathbf{n}) f_0(\mathbf{r}, \mathbf{v}, t) \quad (40a)$$

$$W_{in} = \oint_{\Delta\Sigma} dS \int d\mathbf{v} \mathbf{v} \cdot \mathbf{n} \theta(\mathbf{v} \cdot \mathbf{n}) f_i(\mathbf{r}, \mathbf{v}, t) \quad (40b)$$

where  $\theta$  is the Heaviside function. The requirement of macroscopic homogeneity permits us to express  $f$  in the form

$$f_0 = \frac{X_0}{V - \Delta V} \varphi_0(\mathbf{v}, t), \quad f_i = \frac{X_i}{\Delta V} \varphi_i(\mathbf{v}, t) \quad (41)$$

with

$$\langle X_0/(V - \Delta V) \rangle = \langle X_i/\Delta V \rangle \quad (42)$$

We now insert relations (39)–(42) into the master equation (38) and sum over the external variables  $X_0, V - \Delta V$ . The term  $\sum_{out} R_{ch}(V - \Delta V)$  gives a vanishing contribution and the remaining terms yield

$$\begin{aligned} & \frac{dP(X_i, \Delta V, t)}{dt} \\ & = R_{ch}(\Delta V) \\ & + \sum_{out} - \oint_{\Delta\Sigma} dS \int d\mathbf{v} \mathbf{v} \cdot \mathbf{n} \theta(-\mathbf{v} \cdot \mathbf{n}) \frac{X_0 + 1}{V - \Delta V} \varphi_0 P(X_i - 1, X_0 + 1, t) \\ & + \oint_{\Delta\Sigma} dS \int d\mathbf{v} \mathbf{v} \cdot \mathbf{n} \theta(\mathbf{v} \cdot \mathbf{n}) \frac{X_i + 1}{\Delta V} \varphi_i P(X_i + 1, \Delta V, t) + \dots \end{aligned} \quad (43)$$

In the second term of the RHS we introduce the decomposition

$$P(X_i, X_0, t) = P(X_i, \Delta V, t)P(X_0, V - \Delta V, t) + g(X_i, X_0, t) \quad (44)$$

where  $g$  is the correlation function between  $\Delta V$  and  $V - \Delta V$ . As a first approximation we shall assume that  $g$  remains small, i.e., that  $\Delta V$  and  $V - \Delta V$  are *statistically independent*. It must be emphasized that this assumption can only hold if  $\Delta V$  is sufficiently small. In particular, it becomes a rigorous consequence of kinetic theory of ideal systems in the limit  $\Delta V \rightarrow 0$ . However, as soon as  $\Delta V$  becomes an appreciable part of  $V$ —meaning that the fluctuation has propagated over a macroscopic distance—the assumption breaks down completely.

Bearing this in mind and utilizing the homogeneity condition (42), we may transform (43) into a *closed* form equation:

$$\begin{aligned} dP(X_i, \Delta V, t)/dt = & R_{\text{ch}}(\Delta V) \\ & + \mathcal{D}\langle X_i \rangle [P(X_i - 1, \Delta V, t) - P(X_i, \Delta V, t)] \\ & + \mathcal{D}[(X_i + 1)P(X_i + 1, \Delta V, t) - X_i P(X_i, \Delta V, t)] \quad (45) \end{aligned}$$

We have introduced the expression

$$\mathcal{D} = \frac{1}{\Delta V} \oint_{\Delta \Sigma} dS \int d\mathbf{v} \mathbf{v} \cdot \mathbf{n} \begin{cases} -\theta(-\mathbf{v} \cdot \mathbf{n}) \langle \varphi_0(\mathbf{v}, t) \rangle \\ \theta(\mathbf{v} \cdot \mathbf{n}) \varphi_i(\mathbf{v}, t) \end{cases} \quad (46)$$

which plays the role of an “effective diffusion frequency” of passage of particles across  $\Delta \Sigma$ . In this respect one may note that the distribution  $f_0$  used in the evaluation of  $W_{\text{out}}$  describes the thermal motion of particles directed toward  $\Delta V$  and coming from a layer of a width  $l$ , of the order of the mean free path of  $X$  species within the reaction medium.<sup>(21)</sup>

Equation (45) provides the desired generalization of the birth and death description. Indeed, if  $\Delta V$  is sufficiently small,  $R_{\text{ch}}(\Delta V)$  could be treated in the same way as in the birth and death formalism.<sup>3</sup> In addition to this, however, one has taken into account explicitly the coupling between  $\Delta V$  and the surrounding “big” system. The birth and death formalism is recovered consistently in the completely local limit  $\Delta V \rightarrow 0$  or [see Eq. (46)]  $\mathcal{D} \rightarrow \infty$ . On the other hand, in the limit  $\mathcal{D} \rightarrow 0$ , i.e.,  $\Delta V \rightarrow \infty$ , the diffusion term disappears, but the birth and death description of  $R_{\text{ch}}(\Delta V \rightarrow \infty)$  becomes inadequate for the reasons developed in Section 3. One can show (see appendix A) that the solution of Eq. (45) for the autocatalytic model (26) no longer presents the pathological properties pointed out in Section 3.

## 5. PROPERTIES OF THE MASTER EQUATION

The most characteristic property of the master equation is its *nonlinearity*, arising through the factor  $\langle X_i \rangle$  on the right-hand side. The latter is due to the

<sup>3</sup> Note that the birth and death assumption would be an inadequate approximation for  $R_{\text{ch}}(V - \Delta V)$ .

passage from a global description to a local one. In this respect, it has the same origin as the nonlinear terms of the kinetic equations of statistical mechanics like the Boltzmann or the Vlasov equations. An alternative way to express this property is that the external environment of  $\Delta V$  has been taken into account in an average fashion and that the macroscopic homogeneity condition (42) has related this average to an average over the small system itself. As we shall see later in this section as well as in a subsequent paper, this “competition” between subsystem and external environment will be responsible for the propagation of fluctuations leading to an instability. The similarity between this description and the Prigogine–Herman theory of vehicular traffic<sup>(22)</sup> should be pointed out.<sup>(17)</sup>

We next turn to the relation between  $\Delta V$  and fluctuations. Essentially, this question is equivalent to the problem of evaluating  $\mathcal{D}$ . According to Eq. (46), this parameter is related to the properties of  $\Delta V$  as well as to the state of the system through the velocity distributions  $\varphi_i$ ,  $\langle \varphi_0 \rangle = \varphi_i$ :

$$\mathcal{D} \simeq (1/\Delta V) \int d\mathbf{v} |\mathbf{v}| \varphi_i(\mathbf{v}) \Delta\Sigma(\mathbf{v}) \quad (47)$$

where  $\Delta\Sigma(\mathbf{v})$  stands for the projection of the surface  $\Delta\Sigma$  on a plane perpendicular to  $\mathbf{v}$ . For an isotropic surface  $\Delta\Sigma(\mathbf{v})$  is constant and equal to the cross section of the surface. Thus

$$\mathcal{D} \simeq (\Delta\Sigma/\Delta V)\eta(T) \quad (48)$$

where  $\eta(T)$  is a function of temperature only,

$$\eta(T) = \int d\mathbf{v} |\mathbf{v}| \varphi_i \quad (49)$$

In a first qualitative estimate applicable to macroscopically homogeneous systems one can approximate  $\varphi_i$  by a Maxwellian distribution. The result is

$$\eta_{\text{eq}}^X(T) = (8kT/\pi m_X)^{1/2} \quad (50)$$

where  $m_X$  is the mass of constituent  $X$ . We may note that this expression is approximately equal to the diffusion coefficient of the  $X$  species divided by the mean free path<sup>(21)</sup>:

$$\eta_{\text{eq}}^X(T) \simeq D_X/l_r^X \quad (51)$$

Thus

$$\mathcal{D} \simeq \frac{\Delta\Sigma}{\Delta V} \frac{D}{l_r} \simeq \frac{D}{ll_r} \quad (52)$$

where  $l$  is a characteristic *coherence length* of the fluctuations. This result can also be recovered from an alternative estimation of  $\mathcal{D}$  using the ideas of generalized hydrodynamics (see Appendix B).

The final step in the determination of  $\mathcal{D}$  is to relate the coherence length  $l$  to the intrinsic properties of the system. This can be done easily in a system where the density fluctuations (not to be confused with the fluctuations in composition) can be neglected.<sup>4</sup> Indeed, in this case the macroscopic homogeneity condition yields

$$N_{\Delta V}/\Delta V = N_0/V = \rho_0 = \text{const} \tag{53}$$

where  $N_{\Delta V}$  and  $N_0$  are, respectively, the total numbers of particles inside  $\Delta V$  and in the entire system. Alternatively, one can say that each subvolume  $\Delta V$  behaves as a closed system. From (53),

$$\Delta V = \rho_0/N_{\Delta V}$$

i.e.,

$$l \propto \rho_0^{1/3} N_{\Delta V}^{-1/3} \tag{54}$$

This argument is no longer satisfactory in the presence of density fluctuations. The extension of the calculations in this case is in progress.

Note that if the system undergoes an instability, at the critical point of the unstable transition  $\mathcal{D}$  will be related to the system's chemical parameters, like the rate constants, etc. In this case, therefore,  $l$  [through Eq. (52)] will be related quantitatively to the rate of growth of the fluctuations. This relation will be expounded in a subsequent paper.

The final point we want to develop in this section concerns the moment equations generated by the master equation (45). Multiplying both sides by  $X$  and  $X^2$  and summing over all values of  $X$ , one finds

$$d\langle X \rangle_{\Delta V}/dt = \sum_X X R_{\text{ch}}(\Delta V) \tag{55}$$

$$d\langle X^2 \rangle_{\Delta V}/dt = \sum_X X^2 R_{\text{ch}}(\Delta V) + 2\mathcal{D}[-\langle \delta X^2 \rangle + \langle X \rangle] \tag{56}$$

where

$$\langle \delta X^2 \rangle = \langle X^2 \rangle - \langle X \rangle^2 \tag{57}$$

We recall that for a Poisson distribution  $\langle \delta X^2 \rangle = \langle X \rangle$ . We see that the first moment equation is independent of  $\mathcal{D}$ , in agreement with the requirement of macroscopic homogeneity. On the other hand, diffusion contributes to the mean square deviation of fluctuations through a term expressing the deviation of the probability distribution function from the Poisson regime. In the limit  $\mathcal{D} \rightarrow \infty$  (completely local description) the diffusion term dominates in (56). The system evolves then to a steady state given by the Poisson distribution.

<sup>4</sup> We are indebted to Dr. Lefever for this remark.

We recover therefore the result of Nicolis and Prigogine<sup>(3,10)</sup> based on the phase space theory of fluctuations.

## 6. CONCLUDING REMARKS

In this paper we developed an analysis of *local* fluctuations occurring spontaneously in a chemically reacting system. The resulting *nonlinear* master equation exhibits quite explicitly the *coherence length* of such fluctuations. In contrast, in the familiar birth and death description one overlooks the local aspect of fluctuations and identifies their coherence length with the dimension of the entire system.

There are two obvious extensions of our analysis: spatially inhomogeneous systems and fluid dynamics. A formulation of the first problem is outlined in Appendix C. Details will be published in due course. The somewhat related problem of fluid dynamical systems is under investigation.

One of the most important predictions of our analysis is that the deviation of the probability distribution of fluctuations from the Poisson regime necessitates the nucleation of fluctuations having a large coherence length. Now the Poisson distribution is a consequence of the grand-canonical distribution,<sup>(1)</sup> that is, a consequence of maintaining, locally, an equilibrium momentum distribution. Thus, a large deviation from the Poisson regime indicates that the fluctuation responsible for it will also induce an appreciable deviation of the local statistical state from the local equilibrium state. In particular, the onset of an instability in an ideal reacting mixture should be accompanied by the appearance of a highly nonequilibrium state within the small volume nucleating the destabilizing fluctuation. Further comments on the onset of instabilities are made in a subsequent paper.

The approach outlined in this paper can be regarded as a natural extension to nonequilibrium situations of the basic ideas developed by Landau<sup>(1)</sup> and recently extended by Wilson<sup>(23)</sup> in the context of equilibrium phase transitions. In the latter case, although the system remains macroscopically homogeneous, one introduces a free energy density related to the coherence length of the fluctuations. The analogy with the picture presented in Section 4 is striking.

Finally, it would be of interest to characterize more precisely the type of stochastic process described by the nonlinear master equation (45). It is likely that this equation belongs to the class of situations referred to by McKean as "nonlinear Markov processes."<sup>(24)</sup> Even if the process remains Markovian, it certainly loses its stationary character. Indeed, one of the transition probabilities now depends on the average value  $\langle X \rangle$ , which is an explicit function of time. Further study of this equation on solvable models is necessary in order to explore its mathematical properties.

**APPENDIX A. EFFECT OF DIFFUSION IN THE AUTOCATALYTIC MODEL (26)**

When diffusion is taken into account, the master equation (29) reads [see also Eq. (45)]

$$\begin{aligned} \frac{dP(X, t)}{dt} = & k_1 A(X - 1)P(X - 1, t) - k_1 AXP(X, t) \\ & + k_2 \frac{(X + 1)(X + 2)}{2} P(X + 2, t) \\ & - k_2 \frac{X(X - 1)}{2} P(X, t) \\ & + \mathcal{D}\langle X \rangle [P(X - 1, t) - P(X, t)] \\ & + \mathcal{D}[(X + 1)P(X + 1, t) - XP(X, t)] \end{aligned} \tag{A.1}$$

where  $X$  and  $A$  denote the number of particles of these species within a small volume  $\Delta V$ .

Introducing the generating function<sup>(7)</sup>

$$f(s, t) = \sum_{X=0}^{\infty} s^X P(X, t), \quad |s| \leq 1 \tag{A.2}$$

we obtain, at the steady state,

$$\frac{k_2}{2}(s + 1) \frac{d^2 f}{ds^2} + (\mathcal{D} - k_1 A s) \frac{df}{ds} - \mathcal{D}\langle X \rangle f = 0 \tag{A.3}$$

together with the boundary conditions

$$\begin{aligned} f(1) &= 1 \quad (\text{normalization}) \\ f(-1) &= \text{finite} \end{aligned} \tag{A.4}$$

The second condition, which was recently suggested in a somewhat different form by Mazo,<sup>(15)</sup> expresses that the difference between the probabilities of having even or odd numbers of particles exists and is finite.

Transforming to the new variable

$$z = (s + 1)(2k_1 A/k_2) \tag{A.5}$$

we obtain

$$z \frac{d^2 F}{dz^2} + \left( \frac{\mathcal{D} + k_1 A}{k_2/2} - z \right) \frac{dF}{dz} - \frac{\mathcal{D}\langle X \rangle}{k_1 A} F = 0 \tag{A.6}$$

together with the conditions

$$F(4k_1 A/k_2) = 1, \quad F(0) = \text{finite} \tag{A.7}$$

The solution of (A.6) satisfying conditions (A.7) is proportional to the confluent hypergeometric function  ${}_1\psi_1$ :

$$F(z) = {}_1\psi_1(a, b, z)/{}_1\psi_1(a, b, 4k_1A/k_2) \quad (\text{A.8})$$

with

$$a = \mathcal{D}\langle X \rangle/k_1A, \quad b = (\mathcal{D} + k_1A)/(k_2/2) \quad (\text{A.9})$$

We now want to show that, thanks to diffusion, solution (A.8) is compatible with a nonvanishing mean value  $\langle X \rangle$ . To this end, we differentiate (A.8) with respect to  $z$  and use the relation<sup>(7)</sup>

$$\langle X \rangle = \left( \frac{df}{ds} \right)_{s=1} = \left( \frac{dF}{dz} \right)_{z=4k_1A/k_2} \frac{2k_1A}{k_2} \quad (\text{A.10})$$

We obtain

$$\frac{k_2\langle X \rangle}{2k_1A} = \frac{a}b \frac{{}_1\psi_1(a+1, b+1, 4k_1A/k_2)}{{}_1\psi_1(a, b, 4k_1A/k_2)} \quad (\text{A.11})$$

Note that this highly nonlinear equation always admits the trivial solution  $\langle X \rangle = 0$ , i.e.,  $a = 0$ . To show the existence of nontrivial solutions we consider the asymptotic limit of a large system:

$$A \rightarrow \infty \\ k_1^{-1}, k_2^{-1} \rightarrow \infty, \quad k_1A = \text{finite}$$

For the purposes of evaluating expression (A.11) in this asymptotic limit we will focus on the  $k_2$  dependence of this expression, keeping  $k_1A$  fixed:

$$\nu = k_2^{-1} \rightarrow \infty$$

$$k_1A = \text{fixed finite quantity} \quad (\text{A.12})$$

We observe that

$$4k_1A/k_2 = \nu\xi, \quad a = \nu\alpha, \quad b - a = \nu\beta \quad (\text{A.13})$$

where the quantities

$$\xi = 4k_1A, \quad \alpha = \mathcal{D}\langle X \rangle/(k_1A/k_2) \\ \beta = \{2(\mathcal{D} + k_1A) - [\mathcal{D}\langle X \rangle/(k_1A/k_2)]\} \quad (\text{A.14})$$

have the following properties: (i) they remain finite as  $\nu \rightarrow \infty$ ; (ii) they are all positive.

To see this, we consider the exact mean value equation at the steady state:

$$k_1A\langle X \rangle - k_2[\langle X^2 \rangle - \langle X \rangle] = 0 \quad (\text{A.15})$$

i.e.,

$$\langle X^2 \rangle = \langle X \rangle(k_1A + k_2)/k_2$$

Now

$$\langle X^2 \rangle \geq \langle X \rangle^2$$



Thus, excluding now the trivial value  $\langle X \rangle = 0$ ,

$$\langle X \rangle \leq (k_1 A + k_2)/k_2 = 1 + (k_1 A/k_2) \quad (\text{A.16})$$

Consequently,

$$\begin{aligned} \alpha &\leq \mathcal{D} + (k_2/k_1 A) = \text{finite} \\ 2(\mathcal{D} + k_1 A) &\geq \beta \geq \mathcal{D} + 2k_1 A - \mathcal{D}(k_2/k_1 A) > 0 \end{aligned} \quad (\text{A.17})$$

This proves properties (i) and (ii) stated above. The latter guarantee the following asymptotic expansion of  ${}_1\psi_1$  in the limit (A.12)<sup>(25)</sup>:

$$\begin{aligned} {}_1\psi_1(a, b, x) &= \frac{\Gamma(b)}{\Gamma(a)\Gamma(b-a)} \left(\frac{2\pi}{\mu}\right)^{1/2} e^{-t_1 x (-t_1)^a} \\ &\times (1 + t_1)^{b-a} [1 + O(\nu^{-1})] \end{aligned} \quad (\text{A.18})$$

where

$$\mu = (1 + t_1)(\alpha + \xi t_1^2) \quad (\text{A.19a})$$

and  $t_1$  is the negative root of

$$\xi t(t+1) - \alpha(t+1) - \beta t = 0 \quad (\text{A.19b})$$

Substituting into Eq. (A.11), we obtain

$$\langle X \rangle = \frac{k_1 A}{k_2} + O(k_2) \times f(k_2, \mathcal{D}) \quad (\text{A.20})$$

This agrees with the solution (28b) of the macroscopic equation of mass balance. Thus, a study of fluctuations taking diffusion into account re-establishes this state, which was suppressed in the usual birth and death master equation.

A corollary of the results reported in this appendix is that the nonlinear master equation for model (26) admits *two* steady state solutions. This contrasts strikingly with the behavior of the birth and death master equations, whose linearity ruled out the possibility of multiple solutions.

Note that the results of this appendix provide no information on the *stability* of the two steady states. This problem can be handled along the lines described in a subsequent paper by Van Nypelseer, Kitahara, and the authors.

It is remarkable that the dominant term in the asymptotic result (A.20) does not depend explicitly on the value of  $\mathcal{D}$ . The latter could be taken, at this final stage, as small as desired. It is necessary to stress, however, that such a limit  $\mathcal{D} \rightarrow 0$  *cannot* be envisaged before the asymptotic limit of the large system,  $\nu \rightarrow \infty$ . Indeed, if that were the case, the parameter  $\alpha$  [Eq. (A.14)] would not remain finite and the asymptotic expansion given in Eq. (A.18) would break down.

## APPENDIX B. AN ALTERNATIVE ESTIMATION OF THE COEFFICIENT $\mathcal{D}$

The contribution of diffusion to the equation of mass conservation of an  $X$  species at a point  $\mathbf{r}$  within  $\Delta V$  reads (see Fig. 1)

$$\partial X/\partial t = -\operatorname{div} \mathbf{J}_{\text{dif}} \quad (\text{B.1})$$

In the absence of macroscopic gradients, the diffusion flux  $\mathbf{J}_{\text{dif}}$  is a purely mechanical quantity. Thus, the transport of matter across  $\Delta\Sigma$  can only be the result of a local fluctuation resulting in a deviation from uniformity in the neighborhood of the point  $\mathbf{r}$ . We now set

$$\mathbf{J}_{\text{dif}} = -D \nabla X + f(\mathbf{r}, t) \quad (\text{B.2})$$

We have added a random term<sup>5</sup> to the systematic part of  $\mathbf{J}_{\text{dif}}$  provided by Fick's law. We integrate (B.2) over  $\Delta V$ , use Gauss' divergence theorem, and assume

$$\int d(\Delta V) f(\mathbf{r}, t) \simeq 0 \quad (\text{B.3})$$

provided the volume  $\Delta V$  is sufficiently large to permit a destructive interference of the random contribution to  $\mathbf{J}_{\text{dif}}$ . The result is

$$dX_i/dt = -(1/\Delta V) D \int_{\Delta\Sigma} (\nabla X) \mathbf{n} \cdot d\mathbf{S} \quad (\text{B.4})$$

According to the mean free path theory of transport phenomena<sup>(21)</sup>

$$(\nabla X)_n \equiv \mathbf{n} \cdot \nabla X \simeq \frac{X_i - X_0}{l_r} = \frac{X_i - \langle X \rangle}{l_r} \quad (\text{B.5})$$

where  $l_r$  is a length related to the mean free path. Substituting into (B.4) and using macroscopic homogeneity, we obtain

$$\frac{dX_i}{dt} = \frac{D \Delta\Sigma}{\Delta V l_r} (X - \langle X \rangle) \quad (\text{B.6})$$

Comparing with (38) to (45), we are led to the following identification:

$$\mathcal{D} \simeq \frac{D \Delta\Sigma}{\Delta V l_r} \simeq \frac{D}{l_r} \quad (\text{B.7})$$

in agreement with Eq. (52).

<sup>5</sup> This term is taken to include all fluctuations *except* those of chemical composition.

### APPENDIX C. INHOMOGENEOUS SYSTEMS

Let

$$J_+^n(\mathbf{R}) = - \int_{\mathbf{v} \cdot \mathbf{n} < 0} d\mathbf{v} \mathbf{v} \cdot \mathbf{n} \langle f_0(\mathbf{R}) \rangle \quad (\text{C.1})$$

$$J_-^n(\mathbf{R}) = \int_{\mathbf{v} \cdot \mathbf{n} > 0} d\mathbf{v} \mathbf{v} \cdot \mathbf{n} \langle f_i(\mathbf{R}) \rangle \quad (\text{C.2})$$

$J_+^n$  and  $J_-^n$  represent, respectively, the average amount of particles entering into or leaving the volume  $\Delta V$  with velocities perpendicular to a surface element in the neighborhood of point  $\mathbf{R}$ . In a macroscopically homogeneous system  $J_+^n = J_-^n$ . The results of Section 4, including the definition (46) of  $\mathcal{D}$ , are then recovered. In a macroscopically inhomogeneous system these two quantities are no longer equal, but differ by an amount corresponding to the diffusion flux of the species considered at point  $\mathbf{R}$ :

$$\mathbf{J}_+ - \mathbf{J}_- = \mathbf{J}_{\text{dif}} \quad (\text{C.3})$$

Thus [see Eq. (40a)]

$$W_{\text{out}} = \oint_{\Delta\Sigma} d\mathbf{S} \cdot (\mathbf{J}_-(\mathbf{R}) + \mathbf{J}_{\text{dif}}(\mathbf{R})) \quad (\text{C.4})$$

The first term of this expression as well as the transition probability  $W_{\text{in}}$  [see Eq. (40b)] can be treated exactly as in Section 4. The result is

$$\oint_{\Delta\Sigma} d\mathbf{S} \cdot \mathbf{J}_-(\mathbf{R}) = \mathcal{D} \langle X_i \rangle, \quad W_{\text{in}} = \mathcal{D} X_i \quad (\text{C.5})$$

In dealing with the contribution of  $\mathbf{J}_{\text{dif}}(\mathbf{R})$  we first recall that

$$\lim_{\Delta V \rightarrow 0} \left\{ \left[ \oint_{\Delta\Sigma} d\mathbf{S} \cdot \mathbf{J}_{\text{dif}}(\mathbf{R}) \right] / \Delta V \right\} = -\text{div } \mathbf{J}_{\text{dif}}(\mathbf{r}) \quad (\text{C.6})$$

where  $\mathbf{r}$  is a point surrounded by  $\Delta\Sigma$  and the minus sign is due to the orientation chosen for the normal  $\mathbf{n}$  (see Fig. 1).

If, on the other hand,  $\Delta V$  is kept finite, Eq. (C.6) will represent a *first approximation* in the sense that it will only give the first term of a Taylor expansion of  $\mathbf{J}_{\text{dif}}(\mathbf{R})$  around the point  $\mathbf{r}$  inside  $\Delta V$ :

$$\begin{aligned} & (1/\Delta V) \oint_{\Delta\Sigma} d\mathbf{S} \cdot \mathbf{J}_{\text{dif}}(\mathbf{R}) \\ &= -\text{div } \mathbf{J}_{\text{dif}}(\mathbf{r}) \\ &+ \text{higher order spatial derivative terms} \end{aligned} \quad (\text{C.7})$$

On the other hand, if the macroscopic inhomogeneities do not vary appreciably over a mean free path  $l_r$ ,  $\mathbf{J}_{\text{diff}}$  could be approximated by Fick's law:

$$\mathbf{J}_{\text{diff}} \simeq -D \nabla \langle X_i \rangle / \Delta V \quad (\text{C.8})$$

Substituting (C.5)–(C.8) into (40a), we obtain

$$W_{\text{out}} = \mathcal{D} \langle X_i \rangle + D \nabla^2 \langle X_i \rangle + \text{higher order terms} \quad (\text{C.9})$$

Both  $\langle X_i \rangle$  and the Laplacian are defined at the point  $\mathbf{r}$  inside  $\Delta V$  according to relation (34).

The master equation now reads

$$\begin{aligned} \frac{\partial P(X_i, \Delta V, t)}{\partial t} = & [\mathcal{D} \langle X_i \rangle + D \nabla^2 \langle X_i \rangle + \dots] \\ & \times (P(X_i - 1, \Delta V, t) - P(X_i, \Delta V, t)) \\ & + \mathcal{D}(X_i + 1)P(X_i + 1, \Delta V, t) - \mathcal{D}X_i P(X_i, \Delta V, t) \\ & + \text{chemical terms} \end{aligned} \quad (\text{C.10})$$

The first two moment equations generated by (C.10) are

$$\partial \langle X \rangle / \partial t = D \nabla^2 \langle X \rangle + \text{chemical terms} \quad (\text{C.11})$$

$$\begin{aligned} \partial (\langle \delta X^2 \rangle - \langle X \rangle^2) / \partial t = & -\mathcal{D}[\langle \delta X^2 \rangle - \langle X \rangle^2] \\ & + \text{chemical terms} \end{aligned} \quad (\text{C.12})$$

In the first relation, we recover the mass balance equation in an inhomogeneous system with the familiar diffusion term [see Eq. (2)]. On the other hand, the second moment equation seems to depend on inhomogeneity *only* through the mean value  $\langle X \rangle$  which is affected according to (C.11). An immediate consequence is that in the absence of chemical reactions the steady state probability distribution will always have a Poisson variance, independently of the local gradients. This conclusion is quite reasonable for an ideal mixture in the absence of convective motion.

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## REFERENCES

1. L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Pergamon Press, Oxford (1959).
2. D. Massignon, *Mécanique Statistique des Fluides*, Dunod, Paris (1957).
3. G. Nicolis and I. Prigogine, *Proc. Nat. Acad. Sci. (U.S.A.)* **68**:2102 (1971).

4. G. Nicolis, M. Malek-Mansour, K. Kitahara, and A. Van Nypelseer, *Phys. Lett.* **48A**:217 (1974).
5. M. Bartlett, *Stochastic Population Models in Ecology and Epidemiology*, Meth. Mon. in Appl. Prob. and Stat. (1960).
6. G. Nicolis and I. Prigogine, in *Proc. Faraday Symposium 9 on the Physical Chemistry of Oscillatory Phenomena*, The Royal Institution, London, (December 1974).
7. D. McQuarrie, *Suppl. Rev. Series in Appl. Prob.*, Methuen, London (1967).
8. G. Nicolis and A. Babloyantz, *J. Chem. Phys.* **51**:2632 (1969).
9. R. Hawkins and S. A. Rice, *J. Theor. Biol.* **30**:579 (1971).
10. G. Nicolis, *J. Stat. Phys.* **6**:195 (1972).
11. G. Nicolis, P. Allen, and A. Van Nypelseer, *Progr. Theor. Phys.* **52**:481 (1974).
12. N. Saito, *J. Chem. Phys.* **61**:3644 (1974).
13. Y. Kuramoto, *Progr. Theor. Phys.* **49**:1782 (1973).
14. A. Nitzan and J. Ross, *J. Stat. Phys.* **10**:379 (1974).
15. R. Mazo, *J. Chem. Phys.*, in press.
16. G. Nicolis, in *Cooperative Phenomena*, H. Haken, ed., North-Holland, Amsterdam (1974).
17. I. Prigogine, G. Nicolis, R. Herman, and T. Lam, *Cooperative Phenomena* **2**:1 (1974).
18. Y. Kuramoto, *Progr. Theor. Phys.* **52**:711 (1974).
19. A. Nitzan, P. Ortoleva, and J. Ross, in *Proc. Faraday Symposium 9 on the Physical Chemistry of Oscillatory Phenomena*, The Royal Institution, London (December 1974).
20. M. Franckson, Mémoire de Licence, Univ. of Brussels (1975).
21. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-uniform Gases*, Cambridge Univ. Press, Cambridge (1960).
22. I. Prigogine and R. Herman, *Statistical Theory of Vehicular Traffic*, Elsevier, New York (1971).
23. D. Widom, *Physica* **73**:107 (1974); K. G. Wilson, *Physica* **73**:119 (1974).
24. H. P. McKean, in *Lecture Series in Differential Equations*, Vol. II, Van Nostrand, Princeton, New Jersey (1969).
25. A. Erdélyi *et al.*, eds., *Higher Transcendental Functions*, Bateman Manuscript Project Vol. I, McGraw-Hill, New York (1953).