Asymptotic Properties of Markovian Master Equations

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Received June 10, 1980

An asymptotic method of analysis of fluctuations in systems far from equilibrium is
developed. A systematic singular perturbative expansion of the equation for the generating
function is set up, using as smallness parameter the inverse of the size of the system. Static
and time-dependent properties are analysed before, near and at a bifurcation point, both
for homogeneous and inhomogeneous fluctuations. The connection with critical phenomena
near equilibrium is also discussed.

I. Introduction

The stochastic description of chemical systems in terms of Birth and Death processes
has flourished considerably in recent years [1, 3]. Such systems have the advantage of
being reasonably tractable and at the same time typical of macroscopic systems which
evolve through local processes, such as reactive or elastic collisions, yet are capable of
exhibiting cooperative behaviour that can lead to self-organisation [1, 2]. In terms of a
deterministic description, a transition to such behaviour is reflected by the appearance
of bifurcating new solutions. There has been considerable work concerning the role
of fluctuations in the neighbourhood of these bifurcation points. Recently a new
method based on the theory of singular perturbations has been applied successfully
to this problem in the case of a cusp bifurcation for homogeneous systems [4], and
subsequently extended to include spatial inhomogeneities [5].

It is the purpose of this paper to develop the physical ideas behind this approach
and to extend its application to a wider range of problems. For homogeneous systems,
it turns out to be a systematic method which allows one to determine asymptotically
for \( V \to \infty \) (\( V \) being the total volume of the system) the dominant contributions to the
Master Equation [3, 6]. The probability distribution is known to be approximatively,
when not in the neighbourhood of a bifurcation point, a Gaussian around the deter-
ministic path [7]. How this result needs to be modified when one is in the neighbour-
hood of a bifurcation point has been studied.

Time-dependent properties of the Master Equation are also considered. It turns
out that, except when macroscopic states coexist, the Master Equation can always
be reduced to a Fokker-Planck equation with constant diffusion. This is equivalent to the Langevin equation usually postulated by phenomenological approaches.

These ideas can be generalized to the case of several variables, in particular to the case of the Multivariate Master Equation describing reaction-diffusion systems [5, 8, 11, 35]. Here one encounters as additional difficulty the finiteness of the cell size. Sufficiently far away from the critical point, the Gaussian approximation is found to be valid and one can formulate a law of large numbers and a central limit theorem. In a small vicinity of the critical point however, only the law of large numbers is expected to remain valid, for the Gaussian approximation can be shown to fail. In this case a Landau–Ginzburg potential is obtainable at the stationary state for systems involving one variable, thus the usual renormalization group techniques can be applied [9].

II. THE MULTIVARIATE MASTER EQUATION

Let \( \bar{x}_i \) be appropriately scaled composition variables of a set of chemically active constituents. Assuming Fickian diffusion in an ideal mixture and constant temperature throughout, the evolution equations of these variables take the form

\[
\frac{\partial}{\partial t} \bar{x}_i = \mathcal{V}_i(\bar{x}_1, \ldots, \bar{x}_n ; \lambda_1, \ldots, \lambda_m) + \mathcal{D}_i \nabla^2 \bar{x}_i .
\]  

(II.1)

\( \mathcal{D}_i \) are diffusion coefficients, \( \mathcal{V}_i \) the overall rate of change of \( \bar{x}_i \) arising from the chemical reactions involving constituent \( i \), and \( \lambda_1, \lambda_2, \ldots, \lambda_m \) a set of control parameters descriptive of the system. Our principal goal in this paper is to analyse the dynamics of fluctuations associated with Eq. (II.1).

The natural approach to this problem is in terms of probability theory. Let \( \{X_{it}\} \) denote the number of particles of species \( i \) in a small volume \( \Delta V_r \), centered at \( r \) where the partition in subvolumes \( \{\Delta V_r\} \) covers the entire reaction space. We want to derive an equation for the multivariate probability distribution \( P(\{X_{it}\}; t) \) without any reference to the microscopic degrees of freedom. To this end, we assume that the set \( \{X_{it}\} \) defines a discrete Markov process in an appropriate state space. The Markovian assumption is motivated by the local character of the equations of evolution (II.1) which allows us to describe the instantaneous state of a small volume within a macroscopic system by the same variables as in equilibrium [10].

These remarks lead to the so-called Multivariate Master Equation:

\[
\frac{d}{dt} P(\{X_{it}\}; t) = \sum_{r : (X_{ir})} W(\{X_{ir}\} | \{X_{it}\}) P(\{X_{ir}\}; t)
\]
\[+ \sum_i \frac{Di}{2d} \sum_{r,t} \{ (X_{it} + 1) P(\ldots, X_{it} + 1, X_{ir} + 1, X_{ir} - 1, \ldots; t) - X_{it} P(\{X_{ir}\}; t) \}
\]  

\[\equiv \sum_r L_{eh}(r) P + \sum_{ri} L_d(r, i) P. \]  

(II.2)
The chemical evolution operator $L_{eh}(r)$ is a local operator defined in each small space cell $r$ within our macroscopic system. It displays the transition rate $W$ characteristic of the reaction kinetics. The diffusion operator $L_d(r, I)$ depends on all $r$ as well as on their first neighbours $I$. It is proportional to the jump frequencies $D_i$ between adjacent cells and depends on the dimensionality $d$. As usual $L_{eh}$ is modelled as a Birth and Death process and $L_d$ as a random walk \[8, 11\].

An essential aspect of Eq. (11.2) is the extensivity of transition probabilities, expressing the physically obvious fact that the rate of a process within a cell of volume $\Delta V$ must be proportional to $\Delta V$ times a suitable function of the intensive variables. In the diffusion part of Eq. (11.2) this property is obviously fulfilled. As for the chemical part we shall impose that

$$W([X_{ir}] | \{X_{ir}\}) = \Delta V \ w([X_{ir}/\Delta V], \{X_{ir}/\Delta V\}, 1/\Delta V). \quad (11.3)$$

The analysis of Eq. (11.2) proves to be difficult due to the large number of variables and due to the absence of any obvious perturbation parameter. Although the diffusion rate is typically much larger than the chemical rate constants, it turns out that it cannot be used as a perturbation parameter as it leads to expansions which diverge term by term in the thermodynamic limit \[12\]. No use either can be made of the cell size. The only criterion at this stage is to choose it so that the system is homogeneous and coherent within each cell.

The correct procedure for analysing Eq. (11.2) based on the macroscopic properties of the whole system would be to start with an arbitrary initial partition into cells and to examine the conditions allowing one to lump together groups of such cells in such a way that the volume of the whole system appears explicitly and can thus be used as a perturbation parameter. So far this scheme has not proved feasible \[58\]. Instead the following approach will be adopted: retain in all calculations those terms dominant in $\Delta V$ while estimating the size of the error. It is expected that these terms will provide a satisfactory description in the following two instances. First, in the vicinity of a bifurcation point long range correlations may arise. As a result, one should be able to increase the size $\Delta V$ of the cells up to macroscopic dimensions. And second, far from bifurcation and in the presence of a single stable state, the nonlinear coupling of the macroscopic degrees of freedom is expected to be irrelevant. The description becomes therefore effectively linear in which case the space scale introduced by a partition to cells is immaterial.

Let us now consider how the dominant part in $\Delta V$ can be extracted. It is known \[3, 6, 14\] that equations such as (11.2) are singular in the limit $\Delta V \to \infty$ and cannot therefore generally be expanded in a series solution involving $(\Delta V)^{-1}$. Furthermore standard approximation techniques such as the mean field hypothesis, where one neglects the effects of spatial fluctuations, or the truncation at second order of the hierarchy of the moment equations may prove unsatisfactory, e.g., in the neighbourhood of the bifurcation point.

The method we have followed is based on a singular perturbation expansion which has the advantage of avoiding the above-mentioned difficulties, and also of being
independent of the number of variables in the Master Equation and of whether or not this equation satisfies detailed balance. Such a method has already been applied to the analysis of spatial fluctuations in the cusp bifurcation [5] and its mean field version has been discussed in the context of bifurcation phenomena [4]. It should also be realized that for spatially homogeneous system, several other approaches [1, 3, 6, 18, 48] have been successful in extracting the asymptotic behaviour of the fluctuations. As we show in this paper, our method allows us to cover all these various situations in a very simple way, in terms of the properties of the generating function. Unfortunately, the analysis of several coexisting states remains open [15].

III. HOMOGENEOUS SYSTEMS—CASE OF ONE VARIABLE

III.A. The Method

To simplify notations we first present the method on the simple example of a one variable system neglecting spatial fluctuations. Moreover we assume that this variable changes by jumps of $\pm 1$. We thus consider the following reaction scheme for the chemical intermediate $X$:

$$Ax + iX \xrightleftharpoons{\ell_{i+1}}^{\ell_i} (i + 1)X, \quad i = 0, 1, \ldots, n,$$  \hspace{1cm} (III.1)

where the concentrations of $A_0$, $A_1$, $\ldots$, $A_n$ are controlled from outside. The corresponding global Master Equation reads

$$\frac{d}{dt} P_X(t) = \lambda(X-1) P_{X-1}(t) - \lambda(X) P_X(t) + \mu(X+1) P_{X+1}(t) - \mu(X) P_{X}(t).$$  \hspace{1cm} (III.2)

Let $\epsilon = 1/V$, $V$ being the total volume of the system. The transition rates $\lambda$ and $\mu$ can be written

$$\lambda(X) = \sum_{i=0}^{n+1} k_i e^{i-1} \frac{X!}{(X-i)!},$$  \hspace{1cm} (III.3)

$$\mu(X) = \sum_{i=0}^{n+1} l_i e^{i-1} \frac{X!}{(X-i)!},$$

where we have introduced the intensive variables

$$k_i = \tilde{k}_i \frac{A_i}{V}, \quad i = 0, 1, \ldots, n$$  \hspace{1cm} (III.4a)

and for convenience of notation

$$l_0 = 0; \quad k_{n+1} = 0.$$  \hspace{1cm} (III.4b)
We will assume that $k_o \neq 0$ and $l_{n+1} \neq 0$ thus excluding the existence of an absorbing state at zero or at infinity. This also guarantees the uniqueness of the solution of (III.2) and the ergodicity of the process for finite $V$ [16]. In the following we will be interested in the thermodynamic limit $V \to \infty$ (or $\epsilon \to 0$). The usual approach to this problem is by introducing the probability densities for the reduced variables [3, 17]

$$x = \frac{X}{V} \approx X \epsilon; \quad u = \frac{X}{V^a}, \quad 0 < a \leq 1,$$

where $X = V \bar{X}$ stands for the macroscopic behaviour and the exponent $a$ describes the way in which the fluctuations broaden around this deterministic path as $V \to \infty$. Here we will apply these same ideas to the scaling of the independent variable $s$ of the generating function $F(s, t)$

$$F(s, t) = \sum_{X=0}^{\infty} s^X P_X(t). \quad |s| \leq 1.$$

which has the advantage of technical simplicity.

Note that $F$ is a convex monotonously increasing function in the interval $s \in [0, 1]$. As a consequence of the drifting of the probability $P$ to ever higher values of $X$ as $V \to \infty$, $F$ will have a singular behaviour in this limit: it will take values appreciably different from zero only in the immediate vicinity of $s = 1$ as it tends to its limiting form $\delta_{s=1}^{\bar{X}}$ (see Fig. 1). In order to explore this vicinity in more detail, we will scale $(s - 1)$ with a suitable power of the volume. This allows a regularisation of the generating function when written in terms of the scaled variable and an identification of the dominant terms in the equation of evolution.

From (III.2) and (III.6) this equation reads

$$\frac{\partial}{\partial t} F(s, t) = (s - 1) \sum_{i=0}^{n+1} (k_i S - l_i) \epsilon^{i-1} s^{i-1} \frac{\partial^i}{\partial s^i} F(s, t). \quad (III.7)$$

Note that all terms in the r.h.s. are in principle of the same order of magnitude despite the presence of the small parameter multiplying the higher derivatives:

$$\epsilon^{i-1} \frac{\partial^i}{\partial s^i} F \bigg|_{s=1} = \epsilon^{i-1} \left( \frac{X!}{(X - i)!} \right) \sim O(\epsilon^{-1}). \quad (III.8)$$
Thus, no straightforward perturbation can be carried out. The same difficulty is encountered in the Kramers–Moyal expansion of the Master Equation \[7\].

In order to proceed further, it will prove convenient to introduce the factorial cumulants \(\Pi_i (i = 1, 2, \ldots, )\) defined as the coefficients of the Taylor expansion for \(\ln F\)

\[
F(s, t) = \exp \left\{ \sum_{i=1}^{\infty} \frac{(s - 1)^i}{i!} \Pi_i \right\}. \tag{III.9}
\]

In particular

\[
\Pi_1 = \langle X \rangle,
\]

\[
\Pi_2 = \langle (\delta X)^2 \rangle - \langle X \rangle,
\]

\[
\Pi_3 = \langle (\delta X)^3 \rangle - 3\langle (\delta X)^2 \rangle + 2\langle X \rangle. \tag{III.10}
\]

As a consequence of the extensivity of the transition probabilities, one can prove that

\[
\Pi_1 \sim O(V), \tag{III.11a}
\]

\[
\Pi_i \lesssim O(V^i). \tag{III.11b}
\]

In the sequel, we will assume that \(F(s, t)\) is analytic in the vicinity of \(s = 1\). This property will prove very important, as it will allow us to put forth a perturbative analysis and to determine the spectral properties of the Master Equation (see Section III.E). A sufficient condition for analyticity of \(F(s, t)\) is that the probability distribution decay at all times at least exponentially fast for large values of \(X\) if this is the case at \(t = 0\). The factorial cumulants \(\Pi_i\) then vary with \(i\) in such a way that there exists a positive number \(q\) such that \(\Pi_i q^{-i/i!}\) remains bounded for \(i \to \infty\). Hence, the Taylor expansion for \(\ln F\) exists (Eq. III.9). A broad class of schemes satisfies this property; however we have been unable to determine the most general class of systems compatible with the above requirement.

As one is interested in the asymptotic behaviour of the system, (III.9) and (III.11) suggest the introduction of a new variable:

\[
\xi = V^a(s - 1); \quad \xi \sim O(1), \quad 0 \leq a \leq 1 \tag{III.12}
\]

and the study of the equation obeyed by the new generating function\(^1\)

\[
F_a(\xi, t) = F(1 + e^a\xi, t). \tag{III.13}
\]

According to the value of \(a\), several cases will be considered.

**III.B. Macroscopic Limit**

We discussed in the last section how the thermodynamic limit \(\epsilon \to 0\) taken prior to the limit \(s - 1 \to 0\) leads to a singular behaviour for the generating function, namely \(F = \delta X^r \) (see Fig. 1). In order to extract the dominant contribution from

\(^1\) Hereafter, we drop the subscript \(a\) in the generating function \(F_a(\xi, t)\).
Eq. (III. 7), we will take here the joint limit $\epsilon \to 0$ and $s - 1 \to 0$, implying for (III.12) the value $a = 1$. One then verifies that $F(\xi, t)$ has the following interesting property:

$$\frac{\partial^j}{\partial \xi^j} F \bigg|_{\xi=0} = V^{-1} \Pi_j \lesssim O(1), \quad j = 1, 2, \ldots$$  \hspace{1cm} (III.14)

One can thus identify the dominant terms in the equation for $F(\xi, t)$, which is easily obtained from (III.7) and (III.13)

$$\frac{\partial}{\partial t} F = \xi \sum_{j=0}^{n+1} (k_j (1 + \epsilon \xi) - l_j)(1 + \epsilon \xi)^{-j-1} \frac{\partial^j}{\partial \xi^j} F. \hspace{1cm} (III.15)$$

To lowest order in $\epsilon$, this reduces to

$$\frac{\partial}{\partial t} F = \xi \sum_{j=0}^{n+1} (k_j - l_j) \frac{\partial^j}{\partial \xi^j} F. \hspace{1cm} (III.16)$$

The meaning of $F$ is easily ascertained on the basis of (III.6) and (III.13) with the use of the Euler–Maclaurin formula:

$$F(\xi, t) \sim \int_{-\infty}^{\infty} (1 + \epsilon \xi)^x P(x, t) \, dx.$$  

Thus

$$F(\xi, t) \sim \int_{0}^{\infty} e^{\epsilon x} P(x, t) \, dx, \hspace{1cm} (III.17a)$$

where we have introduced the probability density of the intensive variable $x$

$$P(x, t) = e^{-1} P_{x^{-1} \epsilon}(t). \hspace{1cm} (III.17b)$$

The scaling (III.12) for $a = 1$ thus amounts to the study of the intensive variable $x = X/V$.

The equation for $P(x, t)$ to lowest order in $\epsilon$ is easily obtained from (III.16) and (III.17)

$$\frac{\partial}{\partial t} P(x, t) = - \frac{\partial}{\partial x} \left( f(x) P(x, t) \right), \hspace{1cm} (III.18a)$$

where we have introduced the polynomial

$$f(x) = \sum_{j=0}^{n+1} (k_j - l_j) x^j. \hspace{1cm} (III.18b)$$

This polynomial is simply the macroscopic rate law for the model (III.1)

$$\frac{d}{dt} \bar{x} = f(\bar{x}). \hspace{1cm} (III.19)$$
A standard initial condition for the Master Equation is to impose the total number of particles \( \bar{X}(t = 0) = \bar{X}_0 = e^{-1} \bar{x}_0 \). Therefore, in terms of the generating function one has \( F(s, t = 0) = S^{x_0} \). To lowest order in \( \epsilon \) this becomes

\[
F(\xi, t = 0) = \exp(\xi \bar{x}_0),
\]

With this initial condition, the solution of (III.16) is

\[
F(\xi, t) = \exp(\xi \bar{x}(t)),
\]

where \( \bar{x}(t) \) obeys (III.19) subject to the initial condition \( \bar{x}(t = 0) = \bar{x}_0 \). In terms of the probability density \( P(x, t) \), this is equivalent to

\[
P(x, t = 0) = \delta(x - \bar{x}_0),
\]

\[
P(x, t) = \delta(x - \bar{x}(t)).
\]

We can thus conclude that in the thermodynamic limit (\( \epsilon \to 0 \)) the stochastic trajectory converges in distribution to the deterministic path, if this is true at the initial time. For finite \( t \) this result is contained in a more general theorem due to Kurtz [17]. It remains valid in the limit \( t \to \infty \) taken prior to the thermodynamic limit, provided that the macroscopic rate equation (III.19) has a globally stable stationary solution, i.e. \( \lim_{t \to \infty} \bar{x}(t) = \bar{x}_s \) independent of the initial condition. In fact, as Eq. (III.16) together with the initial condition (III.20a) constitutes a Cauchy problem [20], the uniqueness of the solution (III.21b) follows for some finite time. This result can be extended to arbitrary long times provided the limit \( t \to \infty \) of the r.h.s. of (III.20b) exists, is time independent and coincides with the stationary solution of (III.16). This clearly covers the case of critical (marginal) stability right at a bifurcation point. In the region where the macroscopic rate equation admits multiple steady states however, this property will break down for \( t \to \infty \).

In principle, it should be possible to calculate corrections to the lowest order results (III.16) and (III.20). We will however proceed in another way. Indeed, the setting up of a perturbation scheme starting from (III.15) does not seem promising since an analytic development of \( F(\xi, t) \) (or \( P(x, t) \)) will only be possible if the initial condition allows such a development. For natural initial conditions such as [6]

\[
P(x, t = 0) = e^{-\epsilon \phi(x, t = 0)}
\]

this is clearly not possible. Only the lowest order in \( \epsilon \): \( \lim_{\epsilon \to 0} P(x, t = 0) = \delta(x - \bar{x}_0) \) and its time evolution according to (III.21b) can be considered. The correction to this result will clearly be nonanalytic. Therefore to go beyond this result, the entire equation (III.15) should be solved.

Note that whatever the value of \( \epsilon \) is it always possible to associate to \( F(\xi, t) \) (or to \( F(s, t) \)) a probability density \( \tilde{P} \) through an integral transform of the kind (III.17a)

\[
F(s, t) = \int_0^\infty e^{(s-1)K} \tilde{P}(K, t) dK.
\]
The connection between $\tilde{P}(K, t)$ and $P_X(t)$ is then given by

$$P_X(t) = \int_0^\infty \frac{K^x e^{-K}}{x!} \tilde{P}(K, t) dK,$$

which is simply the "Poisson representation" of $P_X(t)$ and it is well known that the latter is in general only a quasi probability, to be defined in the complex $K$-plane. This representation can be useful for finding approximate solutions of the Master Equation [18, 19].

III.C. Fluctuations around the Deterministic Path

In this section we show how the correction to the deterministic behaviour can be obtained without running into the difficulties mentioned at the end of Section III.B. From the points raised in Section III.A one expects a spreading of the stochastic values $X_t$ around the deterministic trajectory $\bar{X}(t)$ of the order of $O(V^a)$, with $0 \leq a \leq 1$. Clearly the pertinent variable describing deviations of $O(1)$ will be

$$u = \frac{X_t - \bar{X}(t)}{\sqrt{a}}. \quad (\text{III.24})$$

Subtracting the deterministic quantity $1$ amounts to dividing the generating function by $s^X$ (see also (III.9))²

$$F(s, t) s^{-X} = \sum_{X=0}^\infty s^{X-\bar{X}} P_X(t). \quad (\text{III.25})$$

On the other hand, it is clear from (III.11) that there exists a value of $a \leq 1$, such that the following limits

$$\lim_{\epsilon \to 0} \Pi_j e^{i\alpha} \quad (\text{III.26})$$

exist for all $j = 2, 3, \ldots$, and are different from zero for at least one value of $j$. This specifies entirely the choice of $a$.

From (III.25), (III.26) and the asymptotic behaviour of the probability $P_X(t)$ it is clear that the scaling which regularises $F(s) s^{-X}$ in the limit $\epsilon \to 0$ is

$$\xi = \epsilon^{-a} (s - 1). \quad (\text{III.27})$$

On the basis of (III.25), (III.26) and (III.27) one introduces the scaled generating function $\Psi$

$$\Psi(\xi, t) = F(1 + \epsilon^a \xi, t) (1 + \epsilon^a \xi)^{-\epsilon^{-1}} \quad (\text{III.28})$$

\footnote{In Ref. [5a], the dominant contribution was removed through dividing $F$ by $\exp((s - 1)\bar{X})$. This elimination has, however, the disadvantage that the resulting function can be considered as a generating function of a true probability only in the neighbourhood of a bifurcation point (see the discussion at the end of Section III.B).}
with
\[ \rho_1 = (\partial \Psi/\partial \xi)_{t=0} \sim O(\epsilon^a), \]
\[ \rho_2 = (\partial^2 \Psi/\partial \xi^2)_{t=0} = \langle (\delta \chi)^2 \rangle \epsilon^{2a}(1 + O(\epsilon^a)) \sim O(1), \quad (\text{III.29}) \]
\[ \vdots \]
\[ \rho_j = (\partial^j \Psi/\partial \xi^j)_{t=0} = \langle (\delta \chi)^j \rangle \epsilon^{ja}(1 + O(\epsilon^a)) \sim O(1). \]

The physical meaning of $\Psi$ can be seen as follows. By Euler–MacLaurin's summation formula (III.25) becomes
\[ \Psi(\xi, t) \sim \int_{-\infty}^{+\infty} e^{\xi u} P_a(u, t) \, du, \quad (\text{III.30}) \]
where we have introduced
\[ P_a(u, t) = \epsilon^{-a} P_X(t) \big|_{x=ue^{-a}+\bar{x}}. \quad (\text{III.31}) \]

Therefore it appears that $\Psi(\xi, t)$ is an integral transform (two-side Laplace transform) of the probability density $P(u, t)$ of the scaled variable $u$ (see III.24).

After some algebra, we obtain from (III.15) the following equation for $\Psi$ where only those terms in $\epsilon$ that will turn out to be dominant have been written explicitly
\[ \frac{\partial \Psi}{\partial t} = \xi \left\{ \Psi \epsilon^{-1+2a} \left( \frac{1}{2} \xi Q(\bar{x}) + O(\epsilon^a, \epsilon^{1-a}) \right) \right. \]
\[ + \sum_{k=1}^{n+1} \frac{\partial^k \Psi}{\partial \xi^k} \epsilon^{(k-1)(1-a)} \left( \frac{f^{(k)}(\bar{x})}{k!} + O(\epsilon^a) \right) \bigg\}, \quad (\text{III.32}) \]
where the relation
\[ f^{(k)}(\bar{x}) = \frac{d^k}{d\bar{x}^k} f(\bar{x}) = \sum_{j=k}^{n+1} \frac{j!}{(j-k)!} (k_j - l_j) \bar{x}^{j-k} \quad (\text{III.33}) \]
was used and where we introduced the quantity
\[ Q(\bar{x}) = \sum_{j=0}^{n+1} (k_j + l_j) \bar{x}^j. \quad (\text{III.34}) \]

As one can see in Eq. (III.32), necessarily $a \geq \frac{1}{2}$. For $P(u, t)$, one then finds the following equation to the dominant order in $\epsilon$:
\[ \frac{\partial}{\partial t} P(u, t) = - \frac{\partial}{\partial u} \left( \sum_{k=1}^{n+1} \epsilon^{(k-1)(1-a)} f^{(k)}(\bar{x}) \frac{u^k}{k!} - \frac{1}{2} \epsilon^{2a-1} \frac{\partial}{\partial u} Q(\bar{x}) \right) P(u, t), \quad a \geq \frac{1}{2}. \quad (\text{III.35}) \]

As $Q(\bar{x})$ is positive definite, we have therefore obtained a Fokker–Planck equation.

\* As for $F(\xi, t)$, in the following we will drop the subscript $a$. 

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The page contains detailed mathematical derivations and explanations, including integral transforms and summation formulas. The text is centered around the derivation of a Fokker–Planck equation, with a focus on the physical meaning of the variables and terms involved. The equations are presented in a clear and logical manner, with each step explained to ensure understanding. The use of summation formulas and integral transforms is highlighted, providing a comprehensive view of the mathematical processes involved.
This guarantees that $P(u, t)$ remains non-negative for all $t$ and can thus be considered as a true probability, if this is so at the initial time.

It is also instructive to give the corresponding equation for $P(x, t)$:

$$
\frac{\partial}{\partial t} P(x, t) = - \frac{\partial}{\partial x} \left( f(x) - \frac{1}{2} \epsilon \frac{\partial}{\partial x} Q(x) \right) P(x, t),
$$

which is equivalent to the following Langevin equation [47]:

$$
\frac{\partial}{\partial t} x = f(x) + \epsilon^{1/2} y,
$$

$y$ being a Gaussian white noise defined by

$$
\langle y(t_1)y(t_2) \rangle = Q(x) \delta(t_1 - t_2).
$$

This result establishes, at least to dominant order in $\epsilon$, the validity of the nonlinear Langevin equation with a process-independent noise for all finite time, so long as the initial condition be such that $\frac{1}{2} \leq a < 1$. Its validity for $t \to \infty$ (i.e., at the steady state) is guaranteed only when the deterministic equation has a unique stable stationary solution. Several authors have indeed remarked that it yields results for critical behaviour identical to those obtained from the Master Equation [14, 21]. The validity of a Markov process with continuous realisations (Diffusion process) as an asymptotic representation of the Master Equation for finite times was established by Kurtz [17b]. Using Kurtz' theorems Horsthemke and Brenig [22] derived a Fokker–Planck equation analogous to (III.36) with a process-dependent noise term, i.e., $Q = Q(x)$. However, one can verify that to the dominant order in $\epsilon$ the $x$-dependence of $Q$ is immaterial up to the critical point. Some aspects of the problems beyond the critical point will be discussed in the last section.

Let us now consider the case where $\partial f(x)/\partial x \equiv f'(x)$ is different from zero at the initial time. In addition to the trivial result $a = 1$, one verifies that a non-trivial normalizable solution exists when both terms in the r.h.s. of (III.35) contribute equally, in the limit $\epsilon \to 0$. This yields $a = \frac{1}{2}$. Therefore, to dominant order in $\epsilon$, (III.35) can be rewritten as

$$
\frac{\partial}{\partial t} P(u, t) = - \frac{\partial}{\partial u} \left( f'(x) u - \frac{1}{2} \frac{\partial}{\partial u} Q(x) \right) P(u, t).
$$

The solution of this linear Fokker–Planck equation is a propagating Gaussian distribution provided it is initially Gaussian. The fluctuations $\sigma^2 = \langle (\delta u)^2 \rangle$ are described by the equation:

$$
\frac{d}{dt} \langle (\delta u)^2 \rangle = 2f'(x)\langle (\delta u)^2 \rangle + Q(x).
$$

It is clear that these results cannot in general be extended for all times. Indeed, should $f'(x)$ change sign, the fluctuations will be amplified and another regime reached. In particular, at a critical point, $f'(x)$ vanishes and the Gaussian law breaks down. This will be discussed in the next section.
Let $\bar{x} = \bar{x}_{st}$ be the unique stationary solution of the deterministic equation, and suppose that for some "critical" value of the control parameters we have

$$f(\bar{x}_{st}) = f'(\bar{x}_{st}) = \cdots = f^{(k-1)}(\bar{x}_{st}) = 0,$$

$$f^{(k)}(\bar{x}_{st}) \neq 0$$

for a certain (odd) value $k \geq 1$ (the case where $k = 1$ was considered in the previous sub-section where a Gaussian distribution was shown to result). At such a point one has marginal stability of $\bar{x}$ and hence when the parameters are greater than their critical value, one could have bifurcation (degenerate for $k \geq 5$). For $a = k/(k+1)$, the drift and diffusion terms in Eq. (111.35) are of the same order. Thus, to dominant order in $\epsilon$ the equation becomes (see also Ref. (3))

$$\frac{\partial}{\partial \tau} P(u, \tau) = - \frac{\partial}{\partial u} \left\{ \frac{f^{(k)}(\bar{x}_{st}) u^k}{k!} - \frac{1}{2} \frac{\partial}{\partial u} Q(\bar{x}_{st}) \right\} P(u, \tau),$$

$$\tau = t e^{(k-1)/(k+1)}.$$

At the stationary state, one finds

$$P_{st}(u) = \mathcal{N} \exp \left\{ \frac{f^{(k)}(\bar{x}_{st})}{\frac{1}{2} Q(\bar{x}_{st})} \cdot \frac{u^{k+1}}{(k+1)!} \right\},$$

$\mathcal{N}$ being determined by normalisation. It follows that

$$\lim_{V \to \infty} \langle (\delta X)^2 \rangle V^{-2k/(k+1)} = \langle (\delta u)^2 \rangle = \left( - \frac{1}{2} Q(\bar{x}_{st}) \frac{(k+1)!}{f^{(k)}(\bar{x}_{st})} \right) \frac{\Gamma(3/(k+1))}{\Gamma(1/(k+1))}.$$

These probability densities, for $k > 1$, no longer belong to the class of infinitely divisible laws [23]. The transition to critical behaviour thus implies a radical change, not only in the deterministic but also in the stochastic properties of the system. Intuitively, for the type of system considered here one would expect that an extensive (macroscopic) property $X$ such as the total number of particles of a certain constituent, can be considered as a sum of independent random variables $X_i$ (remember we are dealing with ideal system) each of them pertaining to a small subvolume of the system. Hence one would expect $X$ to be distributed according to a Gaussian law (central limit theorem). That this is no longer so at the critical point means that the system can in no way be subdivided into uncorrelated subsets. This of course reflects the coherence associated with bifurcation.

As an illustration of Eq. (111.41) consider the Schlögl model [24]:

$$f(x) = -x^2 + 3x^2 - (3 + \delta) x + (1 + \delta'),$$

$$Q(x) = x^3 + 3x^2 + (3 + \delta) x + (1 + \delta').$$
For $\delta = \delta' > 0, f'(\bar{x})$ is always different from zero. The stationary solution is $\bar{x}_{st} = 1$ so that
\[
\lim_{V \to \infty} \frac{\langle (\delta X)^2 \rangle}{V} = \frac{4}{\delta} + 1.
\] (III.45)

For $\delta = \delta' = 0, f'(\bar{x})$ and $f''(\bar{x})$ are zero and $f'''(\bar{x}) = -6 \neq 0$, thus
\[
\lim_{V \to \infty} \frac{\langle (\delta X)^2 \rangle}{V^{3/2}} = \frac{I(3/4)}{I(1/4)}
\] (III.46)

These results are exact as has already been shown elsewhere [4].

In order to study the transition from $\langle (\delta X)^2 \rangle \sim O(V)$ (Gaussian regime) to $\langle (\delta X)^2 \rangle \sim O(V^{3/2})$ (critical regime), we consider Eq. (111.35) for $P(u, t)$ for arbitrary $\delta = \delta' \geq 0$ and small $\epsilon$:
\[
0 = -\frac{\partial}{\partial u} \left( -\delta u - \epsilon^{2(1-a)} u^3 - \frac{1}{2} \frac{\partial}{\partial u} \epsilon^{2a-1}(8 + 2\delta) \right) P_{st}(u)
\] (III.47)

having as solution
\[
P_{st}(u) = \mathcal{N} \exp \left\{ -\frac{a^3 - 4a}{4 + \delta} \left( \delta u^{-2(1-a)} \frac{u^2}{2} + \frac{u^4}{4} \right) \right\},
\] (III.48)

hence for large $V$:
\[
\frac{\langle (\delta X)^2 \rangle}{V^{2a}} \sim \frac{\delta}{2} \epsilon^{-2(1-a)} \left\{ \frac{K_{3/4}(\epsilon^{-1} \delta^3/8(4 + \delta))}{K_{1/4}(\epsilon^{-3} \delta^3/8(4 + \delta))} - 1 \right\},
\] (III.49)

where $K_n(Z)$ denotes the modified Bessel function [25]. Depending on whether we take the limit $\epsilon \to 0$ faster or slower than the limit $\delta' \to 0$, we recover the Gaussian ($a = \frac{1}{2}$) or the critical ($a = \frac{3}{2}$) behaviour. For the joint limit $\epsilon \to 0$ and $\delta = \epsilon^{1/2} \delta_1$ with $\delta_1$ finite, we find
\[
\frac{\langle (\delta X)^2 \rangle}{V^{2a}} \sim \frac{1}{2} \delta_1 \epsilon^{-3/2 + 2a} \left\{ \frac{K_{3/4}(\delta_1/32)}{K_{1/4}(\delta_1/32)} - 1 \right\}
\] (III.50)

and consequently $a = \frac{3}{2}$ corresponding to critical behaviour is again recovered. These various possibilities are illustrated in Fig. 2.

III.E. Spectral Properties

It will now be shown how the spectral problem can be discussed on the basis of the analyticity of the function $F(\xi, t)$ around $\xi = 0$ which is guaranteed as long as the probability decreases at least exponentially fast for large values of $X$. For the sake of illustration, we consider the case where the deterministic solution has relaxed to its only stationary value $\bar{x} = \bar{x}_{st}$, and denote by $k$ the first nonvanishing derivative of
FIG. 2. Regime dependence on relative values of $\delta$ vs $\epsilon$, as both decrease to zero.

For the Gaussian case, where $k = 1$, the associated spectral problem can easily be solved as it gives rise to a first-order differential equation. One thus obtains the following eigenfunction corresponding to the eigenvalue $\lambda$

$$\Psi_{\lambda}(\xi) = \xi^{\lambda} f'(\bar{x}_{st}) \exp \left\{ -\frac{1}{4} \frac{Q(\bar{x}_{st})}{f'(\bar{x}_{st})} \xi^2 \right\}$$

and it follows from the analyticity of $\Psi_{\lambda}$ that the spectrum is given by

$$\lambda_n = nf'(\bar{x}_{st}), \quad n = 0, 1, 2, \ldots$$

As $\bar{x}_{st}$ is stable, $f'(\bar{x}_{st}) \ll 0$, hence all the eigenvalues are nonpositive in agreement with a general result concerning Master Equations [16]. This method is restricted to the case of a unique stationary solution (possibly critical) for the deterministic equation. When there is a multiplicity of stationary solutions it is clear that starting from Gaussian distribution ($a = \frac{1}{2}$) centered around one of the stable states the system will relax for $t \to \infty$ to a multimodal distribution ($a = 1$). If we nevertheless apply (III.32) with $a = \frac{1}{2}$ to study the spectral problem, the results can be interpreted as describing the time evolution to a quasi-stationary distribution. Indeed, taking the limit $\epsilon \to 0$ prior to $t \to \infty$, the stable states have been isolated from each other.

Finally suppose that the initial condition corresponds to an unstable stationary
solution of the deterministic equations. In this case \( f'(x_{st}) > 0 \), consequently \( \lambda_n > 0 \)
which is in disagreement with a general property of the Master Equations [16].
However, this contradiction is clearly related to the fact that in the limit \( t \to \infty \),
Eq. (III.51) leads to a nonphysical solution, e.g., having negative variances. In this
case (III.51) is valid only for finite values of \( t \) and to obtain the spectral properties
of the problem requires retaining terms of higher order in \( \epsilon \) in (III.32).
Generally speaking it can be shown [26] that in all cases one has

\[
\lambda_n = -n |f'(x_{st})|, \tag{III.54}
\]

An important consequence of this result is that as one approaches a state of critical
stability \( (f'(x_{st}) \to 0) \), the separation between consecutive eigenvalues becomes
increasingly small until at the critical point, the spectrum is continuous. In this case
the eigenvalue problem is best studied on Eq. (III.35). Let all derivatives of order
less than \( k \) (odd) vanish; then to dominant order in \( \epsilon \), the eigenvalue problem becomes
\( \lambda \sim k/(k+1) \)

\[
A_n P_n = -\theta \frac{\partial}{\partial u} (u^k P_n) + \gamma \frac{\partial^2}{\partial u^2} P_n, \tag{III.55}
\]

where

\[
\theta = \frac{f^{(k)}(x_{st})}{k!}, \quad \gamma = \frac{1}{2} Q(x_{st}), \tag{III.56}
\]

Substituting

\[
P_n = \exp \left\{ \frac{\theta}{2\gamma} \frac{u^{k+1}}{k+1} \right\} Y_n, \tag{III.57}
\]

we obtain

\[
\frac{d^2}{du^2} Y_n - \left( \frac{A_n}{\gamma} + \frac{\theta^2}{4\gamma^2} u^{2k} + k \frac{\theta}{2\gamma} u^{k-1} \right) Y_n = 0. \tag{III.58}
\]

As \( \lambda_n = A_n \epsilon^{(k-1)/(k+1)} \), the calculation of the spectral density in the open interval
\( J_0, \infty \) requires the knowledge of the asymptotic behaviour of \( A_n \) for large \( n \), and this
can be obtained by the usual WKB approximation [29]

\[
\int_{\mu_n}^{u_2} \left( \mu_n - \frac{\theta^2}{4\gamma^2} u^{2k} - k \frac{\theta}{2\gamma} u^{k-1} \right)^{1/2} du \sim \left( n + \frac{1}{2} \right) \pi, \tag{III.59}
\]

where \( \mu_n = -(1/\gamma) A_n \) and the bounds of the integral are the zeroes of the integrand.
As \( |\mu_n| \) is large, these roots can be approximated by \( \pm(4\gamma^2 \mu_n/\beta_0)^{1/2k} \); hence by putting

\[
u = (4\gamma^2 \mu_n/\beta_0)^{1/2k}, \tag{III.60}
\]
we get

\[
(4\gamma^2/\theta^2)^{1/2k} \mu_n^{(k+1)/2k} \int_{-1}^{1} \left( 1 - \nu^{2k} - \nu^{k-1} \frac{k\theta}{2\gamma} (4\gamma^2/\theta^2)^{(k-1)/2k} \mu_n^{-(k+1)/2k} \right)^{1/2} d\nu
\]

\[
\sim \left( n + \frac{1}{2} \right) \pi. \quad (III.61)
\]

As \( |\mu_n|^{-(k+1)/2k} \ll 1 \), the last term in the integrand is negligible and one finds

\[
\mu_n^{(1+k)/2k} \left( \frac{2\gamma}{|\theta|} \right)^{1/k} \int_{-1}^{1} \sqrt{1 - \nu^{2k}} d\nu \sim n\pi \quad (III.62)
\]

whence

\[
\lambda_n \sim -\frac{1}{2} e^{(k-1)/(k+1)} n^{2k/(k+1)} \left( \frac{2\pi}{B_k} \right)^{2k/(k+1)} Q(\bar{x}_{st}) \frac{(-f^{(k)}(\bar{x}_{st})/k) Q(\bar{x}_{st})^{2/(k+1)}}{Q(\bar{x}_{st})^{2/(k+1)}}, \quad (III.63)
\]

where

\[
B_k = 4 \int_{0}^{1} \sqrt{1 - \nu^{2k}} d\nu. \quad (III.64)
\]

This result has already been obtained by Matsuo [26]. The point to be made here is that (III.63) follows straightforwardly from Eq. (III.58), which is itself the result of our perturbative analysis of the Master Equation at the generating function level.

The initial value problem is of considerable interest [30, 36, 37, 51]. Within the framework of our method the analysis remains straightforward as long as we keep to the Gaussian regime \( (a = \frac{1}{2}, \text{ see Eq. (III.38)}) \) At the critical point \( (a = \frac{3}{2}) \) and in the region of bistability the situation is much more involved, as the value of the scaling exponent \( a \) will not be maintained between an initial Gaussian distribution and the final state, Eq. (III.42). This raises the question of matching of different regimes which, despite significant progress [14, 41, 51], has not so far been answered in an exhaustive way.

**IV. HOMOGENEOUS SYSTEMS—CASE OF TWO COUPLED VARIABLES**

As an example of a system which does not satisfy detailed balance, we choose a chemical model leading to time symmetry breaking with the appearance of a limit cycle, namely the "Brusselator" [1]:

\[
A \xrightarrow{k_1} X,
\]

\[
B + X \xrightarrow{k_2} Y + D,
\]

\[
2X + Y \xrightarrow{k_3} 3X,
\]

\[
X \xrightarrow{k_4} E. \quad (IV.1)
\]
The macroscopic evolution equations for the concentrations $\bar{x}$ and $\bar{y}$ read

\[ \frac{d\bar{x}}{dt} = \bar{x} \bar{y} - (\beta + 1) \bar{x} + \alpha = f(\bar{x}, \bar{y}), \tag{IV.2} \]

\[ \frac{d\bar{y}}{dt} = -\bar{x} \bar{y} + \beta \bar{x} = g(\bar{x}, \bar{y}), \]

where we set

\[ k_1 = k_4 = 1, \quad k_2 = V^{-1}, \quad k_3 = V^{-2}, \tag{IV.3} \]

\[ \alpha = \frac{A}{V} \quad \text{and} \quad \beta = \frac{B}{V}. \]

It is well known that this set of equations leads to limit cycle behaviour for values of $\beta$ such that $\beta > \beta_c$, with

\[ \beta_c = \alpha^a + 1. \tag{IV.4} \]

Following the method expounded in Section III.A, it is easily found that the stochastic and macroscopic paths coincide in the thermodynamic limit. In order to discuss the fluctuations we introduce in analogy with (III.6), (III.12) and (III.28)

\[ F(s_x, s_y, t) = \sum_{X=0}^{\infty} \sum_{Y=0}^{\infty} s_x^X s_y^Y P_X, \gamma(t), \]

\[ \xi = (s_x - 1) e^{-a}, \]

\[ \eta = (s_y - 1) e^{-b}, \tag{IV.5} \]

\[ \Psi(\xi, \eta, t) = F(s_x, s_y, t) s_x^{-\xi} s_y^{-\eta}, \]

where $P_{X,\gamma}(t)$ stands for the probability for $X, Y$ obeying the usual (global) Birth and Death Master Equation corresponding to reaction scheme (IV.1).

For $a = b = \frac{1}{2}$ (Gaussian regime) we obtain to dominant order in $\epsilon$ the following equation for $\Psi$ (compare with Eq. (III.51)):

\[ \frac{\partial}{\partial t} \Psi = \Psi(Q_{xx}\xi^a + 2Q_{xy}\xi\eta + Q_{yy}\eta^b) \]

\[ + \frac{\partial \Psi}{\partial \xi} (\xi f_x + \eta g_x) + \frac{\partial \Psi}{\partial \eta} (\xi f_y + \eta g_y), \tag{IV.6} \]

where the lower index in $f$ and $g$ denotes differentiation with respect to that variable. The noise terms $Q$ are given by

\[ Q_{xx} = \bar{x} \bar{y} + \beta \bar{x} + \bar{x} + \alpha, \]

\[ Q_{yy} = \bar{x} \bar{y} + \beta \bar{x}, \tag{IV.7} \]

\[ Q_{xy} = Q_{yx} = -(\bar{x} \bar{y} + \beta \bar{x}). \]
Equation (IV.6) admits solutions of the type
\[ \Psi = \exp \left\{ \sigma_{xx} \frac{x^2}{2} + \sigma_{yy} \frac{y^2}{2} + \sigma_{xy} xy \right\}, \tag{IV.8} \]
where the fluctuations obey the following equation [28]:
\[ \frac{d}{dt} \begin{pmatrix} \sigma_{xx} \\ \sigma_{xy} \\ \sigma_{yy} \end{pmatrix} = \begin{pmatrix} 2f_x & 0 & 2f_y \\ g_x & f_y & 0 \\ 0 & 2g_y & 2g_x \end{pmatrix} \begin{pmatrix} \sigma_{xx} \\ \sigma_{xy} \\ \sigma_{yy} \end{pmatrix} + \begin{pmatrix} Q_{xx} \\ Q_{xy} \\ Q_{yy} \end{pmatrix}. \tag{IV.9} \]

These equations describe the evolution of the probability starting from a Gaussian distribution, for finite times. They remain valid at the stationary state \((t \to \infty)\) only before bifurcation. One then obtains:
\[ \sigma_{xx}^{st} = V^{-1}\langle (\delta X)^2 \rangle = \alpha \frac{\beta_e + \beta}{\beta_e - \beta}, \tag{IV.10} \]
\[ \sigma_{yy}^{st} = V^{-1}\langle (\delta Y)^2 \rangle = \alpha \frac{\beta e + \beta}{\beta e - \beta}, \]
\[ \sigma_{xy}^{st} = V^{-1}\langle (\delta X) (\delta Y) \rangle = -\frac{2\alpha \beta}{\beta e - \beta}. \]

We now illustrate how the spectral properties can be easily deduced from the analyticity of \(\Psi(\xi, \eta)\) near the origin, in the case of relaxed deterministic values. From (IV.6) we obtain the following eigenvalue problem
\[ \lambda \phi_\lambda = \left\{ \left( (\beta - 1) \xi - \beta \eta \right) \frac{\partial}{\partial \xi} + \alpha^2 \left( \xi - \eta \right) \frac{\partial}{\partial \eta} \right\} \phi_\lambda , \tag{IV.11} \]
where we have introduced
\[ \phi = \Psi/\Psi_{st} \tag{IV.12} \]
and \(\Psi_{st}\) is the zero eigenfunction
\[ \Psi_{st} = \exp \left( \sigma_{xx}^{st} \frac{x^2}{2} + \sigma_{yy}^{st} \frac{y^2}{2} + \sigma_{xy}^{st} xy \right). \tag{IV.13} \]

The general solution of the partial differential equation (IV.11) reads
\[ \phi_\lambda = \left( \eta - \frac{\alpha^2 + \beta}{\beta} \xi \right)^{-\lambda/\beta} \Phi(C_+/C_-), \tag{IV.14} \]
with
\[ C_\pm = \left( \eta - \xi \frac{\alpha^2 + \rho_\pm}{\xi} \right)^{1/(\alpha^2)} \]  
(IV.15)

and
\[ \rho_\pm = -\frac{1}{2}(\beta_c - \beta) \pm \frac{1}{2}((\beta_c - \beta)^2 - 4\alpha^2)^{1/2} \pm i \]  
(IV.16)

The analyticity of \( \phi \) then implies
\[ \lambda_{n,m} = (n + m)R + (n \pm m)I; \quad n, m = 0, 1, \ldots \]  
(IV.17)

Note that as \( \beta \uparrow \beta_c \), the real part of the eigenvalues \( \lambda_n \) goes to zero. However an imaginary part subsists which is precisely the frequency \( \alpha \) of the limit cycle at the bifurcation point, together with its harmonics.

A detailed discussion of the eigenvalue problem as well as the properties of the stationary solution of the Master Equation at and beyond the bifurcation point is considerably more involved and is reported elsewhere [13, 27, 59].

V. INHOMOGENEOUS SYSTEMS

V.A. Mean-Field Description and Critical Dimensionality

In the previous sections we illustrated our development on a contracted form of the Master Equation, where it was assumed that all spatial fluctuations are wiped out by an efficient mechanism of stirring. Now, we come to the problem of fluctuations including spatial inhomogeneities.

The absence in the Multivariate Master Equation of an evident asymptotic element related to the increase of the system's size (thermodynamic limit) was pointed out in Section II (see also [31, 32, 52]). However, for a finite system of volume \( V \), a systematic perturbation scheme was set up, based on the smallness of the ratio \( \tau_D/\tau_{ch} \), where \( \tau_D \) and \( \tau_{ch} \) are the characteristic times for diffusion and chemical reaction, respectively. It was proved that in the limit of this ratio going to zero, the multivariate probability assumes the following form [12, 32].

\[ P(\{X_r\}; t) \to P_x(t) \frac{X!}{\prod_r X_r!} \left( \frac{\Delta V}{V} \right)^X, \quad X = \sum_r X_r, \]  
(V.1)

where \( X_r \) denotes the number of particles in the cell labelled by \( r \) and \( P_x(t) \) is the global probability distribution obeying the Master Equation (III.2). The above limit expressing the predominance of diffusion over chemical reaction leads thus to mean field results. It turns out that, in general, this conclusion cannot be extended to the thermodynamic limit \( V \to \infty \) (with fixed cell size \( \Delta V \)), since the characteristic diffusion
time increases for inhomogeneities of increasing wavelength. In fact, it is easy to
verify that [33]
\[ \frac{1}{\tau_D} \sim D V^{-2/d}. \]  
where \( D \) is Fick's diffusion coefficient and \( d \) the dimensionality of the system. In the
absence of critical phenomena, it is clear that for some finite volume of the system,
the characteristic diffusion and chemical times will be of the same order and as a result
the above perturbation development will cease to be valid. On the other hand, in the
case of critical behaviour the chemical process will be characterised by a critical
slowing down. Indeed, in the previous section we established that for \( k \)-valued
critical points, with \( \bar{x} = \bar{x}_{st} \), the inverse characteristic chemical time is given by
(see Eq. (III.41)):
\[ \frac{1}{\tau_{ch}} \sim \kappa V^{-(k-1)/(k+1)}, \]  
where \( \kappa \) is a typical chemical constant.

Now, from Eq. (V.2) it is clear that the rate of increase of the characteristic diffusion
time \( \tau_D \) for \( V \to \infty \) slows down as the dimensionality becomes larger. Thus, there
exists a critical dimensionality
\[ d_c = 2 \frac{k + 1}{k - 1} \]  
for which the characteristic reaction and diffusion times are of the same order in \( V \).
For higher dimensionalities \( d > d_c \), diffusion will be dominant and the multivariate
distribution will relax to the diffusional equilibrium form (V.1); hence mean field
behaviour will result. For \( d < d_c \), diffusion is not strong enough to correlate the cells
perfectly and nonclassical behaviour is expected (critical behaviour may even be ruled
out).

In the following it will be shown how our development allows one to recover the
above physical arguments.

V.B. General Formulation

We investigate here the consequence of considering the inverse cell size \( \epsilon \equiv 1/\Delta V = l^{-d} \) as a small parameter\(^4\) in the MME (II.2). The validity of this Ansatz was discussed
in Section II. Following the arguments of Section III.B, we introduce the generating
function
\[ F(\{\xi_r\}, t) = \sum_{(X_r)} \prod_r s_r^{X_r} P(\{X_r\}, t) \bigg|_{s_r = \epsilon \delta_{r+1}}, \]  
which is supposed to be analytic in the vicinity of \( s_r = 1 \) or \( \xi_r = 0 \) (see discussion in

\(^4\) In this section, the total volume of the system will always be represented by \( V \), \( \epsilon \) referring only
to the inverse cell size \( 1/\Delta V \).
Section III.C. Performing the perturbative expansion described in Section III.B, we find that \( F \) obeys to dominant order in \( \epsilon \) (compare with (III.16))

\[
\frac{\partial F(\{\xi_r\}, t)}{\partial t} = \sum_r \left[ \xi_r \sum_{j=0}^{n+1} (k_j - l_j) \frac{\partial}{\partial \xi_r} + \frac{D}{2d} \sum_r \left( \frac{\partial}{\partial \xi_{r+1}} - \frac{\partial}{\partial \xi_r} \right) \right] F(\{\xi_r\}, t), \tag{V.6}
\]

where the sum \( \sum_r \) runs over all nearest neighbours. For the standard initial condition

\[
F(\{\xi_r\}, t = 0) = \exp \left\{ \sum_r \xi_r \bar{x}_r(t = 0) \right\} \tag{V.7a}
\]

the solution reads

\[
F(\{\xi_r\}, t) = \exp \left\{ \sum_r \xi_r \bar{x}_r(t) \right\}, \tag{V.7b}
\]

where \( \bar{x}_r(t) \) obeys the deterministic reaction diffusion equation (discrete in space)

\[
\partial_r \bar{x}_r = f(\bar{x}_r) + \frac{D}{2d} \sum_r (\bar{x}_{r+1} - \bar{x}_r). \tag{V.8}
\]

The stochastic trajectory thus converges in distribution to the deterministic path. This result was also obtained, from a quite different point of view, in Ref. [32].

In order to study the fluctuations, we introduce (compare with (III.28))

\[
\Psi(\{\xi_r\}, t) = \left. \frac{F(\{\xi_r\}, t)}{\prod_r \delta_{\xi_r - \bar{x}_r}} \right|_{\bar{x}_r = \bar{x}_{r+1}}. \tag{V.9}
\]

Similarly to Section III, one can show that \( \Psi(\{\xi_r\}; t) \) is related to the multivariate probability density \( P((u_r); t) \) by

\[
\Psi(\{\xi_r\}; t) = \int_{-\infty}^{+\infty} \prod_r d u_r \exp \left\{ \sum_r \xi_r u_r \right\}, \tag{V.10}
\]

where

\[
u_r = (X_r - \bar{X}_r)/\Delta V^a = \epsilon^{-1+a}(x_r - \bar{x}_r). \tag{V.11}
\]

In the most general case the equation for \( \Psi \) to dominant order in \( \epsilon \) for \( 0 < a < 1 \) reads (see also Eq. (III.32))

\[
\frac{\partial \Psi}{\partial t} = \sum_r \xi_r \left\{ \Psi e^{-1-2a} \left( \frac{1}{2} \xi_r Q(\bar{x}_r) + O(\epsilon^a, \epsilon^{1-a}) \right) \right.
\]

\[
+ \sum_{k=1}^{n+1} \frac{\partial^k \Psi}{\partial \xi_r} e^{(k-1)(1-a)} \left( \frac{1}{k!} f^{(k)}(\bar{x}_r) + O(\epsilon^a) \right) \bigg\}
\]

\[
+ \frac{D}{2d} \sum_{r,t} \xi_r \left\{ \left( \frac{\partial \Psi}{\partial \xi_{r+1}} - \frac{\partial \Psi}{\partial \xi_r} \right) + \Psi e^{-1-2a} \left( \frac{1}{2} \xi_r (\bar{x}_{r+1} - \bar{x}_r) \right. \right.
\]

\[
- (\xi_{r+1} - \xi_r \bar{x}_r) + O(\epsilon^a) \bigg\} \bigg|_{\bar{x}_r = \bar{x}_{r+1}}. \tag{V.12}
\]
This equation contains two parts reflecting respectively the chemical (Birth and Death) and diffusion (random walk) processes. As we shall see later, all properties of the system near the bifurcation point are governed by the competition between these two processes.

From (V.12) it is easy to derive the equation for the probability density \( P(u_t; t) \). In terms of the intensive variables \( \{x_i\} = \{X_i/\Delta V\} \), one obtains

\[
\frac{\partial}{\partial t} P(x_i; t) = -\sum_r \frac{\partial}{\partial x_i} \left\{ f(x_i) + \frac{D}{2d} \sum_t (x_{r+t} - x_i) \right\} P

+ \frac{\varepsilon}{2} \sum_{r,r'} \frac{\partial^2}{\partial x_i \partial x_{r'}} \left\{ Q(x_i) \delta_{r,r'} + \frac{D}{2d} \sum_t ((x_{r+t} - x_i) \delta_{r,r'}

- (\delta_{r,r'} \delta_{r,r'} - \delta_{r,r'})(\bar{x}_r + \bar{x}_{r'})) \right\} P.
\]

This is a Fokker–Planck equation with nonlinear drift and with constant (i.e., process independent) diffusion. It is equivalent to the following Langevin equation

\[
\frac{\partial}{\partial t} x_i = f(x_i) + \frac{D}{2d} \sum_t (x_{r+t} - x_i) + \varepsilon^{1/3} F_i(t),
\]

where \( F_i(t) \) is a “multi-Gaussian white noise” defined by

\[
\langle F(t) F(t') \rangle = \delta(t - t') \left\{ Q(x_i) \delta_{r,r'}

+ \frac{D}{2d} \sum_t ((x_{r+t} - x_i) \delta_{r,r'} - (\delta_{r,r'} \delta_{r,r'} - \delta_{r,r'})(\bar{x}_r + \bar{x}_{r'})) \right\}.
\]

This is the discretized version of the well-known results [38, 54–56]:

\[
\langle F(r, t) F(r', t) \rangle = \delta(t - t') \left( \delta(r - r') Q(x(r, t)) + 2D \frac{\partial}{\partial r} \frac{\partial}{\partial r'} \bar{x}(r, t) \delta(r - r') \right),
\]

where we have set

\[
\varepsilon^{1/3} F_i(t) = F_i(t)
\]

and used the connection between the mean jump frequency \( D \) and the Fick's diffusion coefficient \( D \):

\[
D = \frac{1}{2d} l^2 D \equiv \frac{\varepsilon^{-2/d}}{2d} D.
\]

These results establish the validity of the nonlinear Langevin equation with a process-independent noise for all finite time, if it is so initially. Its validity for \( t \to \infty \) (i.e.,
at the steady state) is guaranteed only when the deterministic equation has a unique stable stationary solution. This is true before and at the bifurcation point.

Note that the strength of the noise $Q$ arising from the chemical process is evaluated along the deterministic path. The noise contribution arising from the diffusion gives rise to nondiagonal terms $\left( \frac{\partial^2}{\partial x_r \partial x_{r'}} \frac{\partial}{\partial r}, r \neq r' \right)$ in the Fokker-Planck equation (V.13). This makes the analysis of the latter equation extremely complex, except in the following two instances: near the bifurcation point where the diffusion contribution to the noise term proves to be negligible (see below and Ref. [57]), and far before the bifurcation point where only the linear term in $f(x_r)$ is relevant for all practical purposes. These two cases will now be treated separately.

V.C. Central Limit Theorem and Eigenvalue Problem

We will consider the spectral problem associated with Eq. (V.12) for $|f'(\bar{x}_{st})| \gg O(\epsilon^{1/2})$, that is sufficiently far from bifurcation point ($f'_{st} < 0$). In this case Eq. (V.12) admits a normalisable nontrivial steady state solution, in the limit $\epsilon \to 0$, only for the value $a = \frac{1}{2}$. It then reduces to a first-order partial differential equation which can be solved straightforwardly. For the stationary solution (zero eigenfunction) one finds

$$\Psi_{st}(\{\xi_r\}) = \exp \left\{ \frac{1}{2} \sum_{r, r'} g_{r, r'} \xi_r \xi_{r'} \right\} , \tag{V.18a}$$

where the correlation functions $g_{r, r'}$,

$$g_{r, r'} = g_{r', r} = \left. \frac{\partial \Psi}{\partial \xi_r \partial \xi_{r'}} \right|_{\{\xi_r = 0\}} = \epsilon \langle \delta X_r \delta X_{r'} \rangle (1 + O(\epsilon^{1/2})) \tag{V.18b}$$

obey the following set of equations:

$$\frac{D}{2d} \sum_{l} \left( (g_{r+\ell, r'} - \bar{x}_{st} \delta_{r+\ell, r'}) - (g_{r, r'} - \bar{x}_{st} \delta_{r, r'}) \right)$$

$$+ f'(\bar{x}_{st})(g_{r, r'} - \bar{x}_{st} \delta_{r, r'}) + \left( \frac{1}{2} Q(\bar{x}_{st}) + \bar{x}_{st} f'(\bar{x}_{st}) \right) \delta_{r, r'} = 0. \tag{V.19}$$

These equations can be solved by lattice Fourier transformation [12]. The resulting correlation function is of the Ornstein–Zernike [34] type and displays a classical divergence of the correlation length as $|f'(\bar{x}_{st})|^{-1/2}$. In terms of the intensive variables $x_r = X_r / AV$, one obtains from (V.18)

$$P_{st}(\{x_r\}) \sim \exp \left\{ - \frac{\epsilon^{-1}}{2} \sum_{r, r'} (g^{-1})_{r, r'} (x_r - \bar{x}_{st})(x_{r'} - \bar{x}_{st}) \right\} , \tag{V.20}$$

which is a multi-Gaussian distribution. Note the correlation between cells as a consequence of their coupling through diffusion.

\footnote{Note that at the thermodynamic equilibrium, $\frac{1}{2} Q_{st} + \bar{x}_{st} f'_{st} = 0$. Hence Poissonian behaviour is recovered: $g_{r, r'} = \bar{x}_{st} \delta_{r, r'}$.}
Let us now focus our attention on the stochastic properties of the total number $X$ of particles. This quantity is the sum of the correlated random variables $X_r$: $X = \sum_r X_r$.

The generating function $\Psi_{\xi}(\xi, x)$ corresponding to the probability for $X$ is obtained from the multivariate function $\Psi((\xi_\tau), t)$ by putting all $\xi_\tau$ equal to $\xi$. One then finds at the stationary state:

$$\Psi_{\xi}(\xi) = e^{\sigma^2 \xi^2/2},$$

where

$$g = \epsilon \sum_{r, r'} \langle \delta X_r, \delta X_r' \rangle = \epsilon \langle (\delta X)^2 \rangle = \frac{1}{2} \left( \frac{Q(\bar{x}_{\mathrm{st}})}{f'(\bar{x}_{\mathrm{st}})} \right) \frac{V}{dV}.$$  \hfill (V.21b)

The probability distribution for the total number $X$ is thus Gaussian:

$$P_{\mathrm{st}}(X) \sim \exp \left( -\frac{(X - \bar{X}_{\mathrm{st}})^2}{2\langle (\delta X)^2 \rangle} \right).$$  \hfill (V.22)

We have therefore derived a central limit theorem. Note that this result breaks down in the vicinity of the bifurcation point, that is when $f'(\bar{x}_{\mathrm{st}}) \to 0$. The result (V.22) is in accordance with the global description (see (III.42)).

Let us now consider the problem of the nonzero eigenvalues $\lambda$ to be determined from

$$\lambda \Psi_\lambda = \sum_r \xi_r \left\{ \frac{1}{2} Q(\bar{x}_{\mathrm{st}}) \xi_r + f'(\bar{x}_{\mathrm{st}}) \frac{\partial}{\partial \xi_r} \right\} \Psi_\lambda$$

$$+ \frac{D}{2d} \sum_{r, r'} \xi_r \left\{ \left( \frac{\partial}{\partial \xi_{r+r'}} - \frac{\partial}{\partial \xi_r} \right) - \bar{x}_{\mathrm{st}} (\xi_{r+r'} - \xi_r) \right\} \Psi_\lambda$$

( V.23)

together with the property of the analyticity of $\Psi_\lambda$ in the neighbourhood of $\{\xi_\tau\} = 0$.

For simplicity, we derive the spectrum in the case of a one-dimensional system ($N$ cells, periodic boundary conditions). The generalisation to higher dimension is straightforward. Setting

$$\Psi_\lambda = \Psi_{\mathrm{st}} \phi_\lambda$$

(V.24)

and introducing the new variables

$$\eta_j = \frac{1}{N} \sum_{k=1}^N \xi_k \exp \left( -\frac{2\pi jk}{N} \right), \quad j = 1, \ldots, N$$

(V.25)

we obtain from (V.23)

$$\lambda \phi_\lambda = \sum_{j=1}^N \left[ f'(\bar{x}_{\mathrm{st}}) + D \left( \cos \frac{2\pi j}{N} - 1 \right) \right] \eta_j \frac{\partial \phi_\lambda}{\partial \eta_j},$$

(V.26)

Clearly the functions

$$\phi_\lambda = \prod_{j=1}^N \eta_j^{l_j}, \quad l_1, \ldots, l_N \in \mathbb{N}$$

(V.27)
span the space of the analytic functions which we consider. They are eigenfunctions of (V.26) corresponding to the degenerate eigenvalues [33]

\[ \lambda = \lambda_{1, \ldots, N} = \sum_{j=1}^{N} \left[ f'_{st} + D \left( \cos \frac{2\pi}{N} j - 1 \right) \right] \lambda_j. \]  (V.28)

The spectral problem near and beyond the bifurcation point (including the effect of inhomogeneous fluctuations) is much more involved and has received no solution so far.

V.D. Critical Behaviour

Near the bifurcation point, the results obtained in the preceding section may be invalidated under the influence of nonlinear chemical modes. Indeed, in this case \( f'(\bar{x}_{st}) \) is small and higher-order partial derivatives involving higher derivatives of \( f(\bar{x}_{st}) \) come into play (see Eq. (V.12)). This implies values of \( a > \frac{1}{2} \), in which case the noise contribution arising from diffusion (i.e., terms in \( \Psi^{-1-2a} \) in the diffusion part of Eq. (V.12)) becomes negligible. The Fokker–Planck Eq. (V.13) takes then the following simple form:

\[ \frac{\partial}{\partial t} P(x; t) = -\sum_{r} \frac{\partial}{\partial x_r} \left\{ f(x_r) + \frac{D}{2d} \sum_{l} (x_{r+l} - x_r) - \frac{1}{2} \varepsilon Q(\bar{x}_r) \frac{\partial}{\partial x_r} \right\} P(x; t), \]  (V.29)

which can be solved exactly at the stationary state; one finds

\[ P_{st}(x_r) \sim \exp \left\{ -\frac{2\varepsilon^{-1}}{Q_{st}} \sum_{r} \left( -\int dx_r f(x_r) + \frac{D}{8d} \sum_{l} (x_{r+l} - x_r)^2 \right) \right\}. \]  (V.30)

Equations (V.13) and (V.30) establish the link between the Master Equation approach and a method which is well known in the analysis of critical phenomena and which has been utilised recently in the context of nonequilibrium phase transitions [21]. Indeed, Eq. (V.30) features the exponential of the Landau–Ginsburg functional, familiar in the theory of critical phenomena [9], and can therefore be studied by renormalization group methods. As it is well known, the result of this analysis is the existence of a critical dimensionality \( d_c \) in agreement with (V.4) and the concomitant appearance of nonclassical exponents describing the divergence of variances, correlation functions, and so forth.

The physical meaning of such critical behaviour can be further clarified by analysing the relative importance of the various terms in Eq. (V.12) without having to construct the explicit form of the solution. To make this clear, let us assume that at the bifurcation point \( (f'_{st} = f''_{st} = 0) \) the third derivative of \( f_{st} \) is strictly negative: \( f'''_{st} < 0 \). This situation is the analogue of a critical point in equilibrium phase transitions. From (V.12) one notes that as \( f'_{st} \to 0 \) the third-order partial derivative, which is responsible for nonlinear coupling of chemical modes, is no longer negligible; this implies \( a = \frac{3}{2} \). The linear and the nonlinear modes are thus comparable in a region around the
bifurcation point whose size is clearly of order $O(\epsilon^{1/2})$ and which therefore can be investigated by setting

$$\delta \equiv -f'_{st} = \delta_1 \epsilon^{1/2}; \quad 0 < \delta_1 < \infty.$$  \hfill (V.31)

Using Eq. (V.17) we can then write the equation for $P(\{u_i\}; t)$ as

$$\epsilon^{-1/2} \frac{\partial}{\partial t} P(\{u_i\}; t) = \sum_r \left\{ - \frac{\partial}{\partial u_i} \left( - \delta_1 u_i - u_i^3 \right) \\
+ D \epsilon^{(4-d)/2d} \sum_i (u_{i+1} - u_i) + \frac{Q_{st}}{2} \frac{\partial^2}{\partial u_i^2} \right\} P(\{u_i\}; t),$$  \hfill (V.32)

where for simplicity we have assumed that $f'_{st} = 0$ and for the convenience of notation we have set $f''_{st} = -1$ (for the case $f''_{st} \neq 0$ see Ref. [5a]). The $\epsilon$-dependence of the diffusion term in (V.32) reflects the relative importance of diffusion versus chemical reactions: these are equally important for a critical dimension $d_c = 4$, in accordance with our previous arguments (see Eq. (V.4)). For $d < 4$, the diffusion term is of lower order in $\epsilon$ than the chemical one. However, because of the finite difference term (which is the discrete analogue of the Laplace operator) involved in the diffusion, the latter is in general a correction which is nonanalytic in $\epsilon$ and hence cannot be a priori neglected, whatever the dimensionality of the system. The stationary solution of (V.32), expressed in terms of the intensive variables $\{x_i\}$ takes now the following form:

$$P_{st}(\{x_i\}) \sim \exp \left\{ - \frac{2\epsilon^{-1}}{Q_{st}} \sum_i \left( \frac{\delta}{2} (x_i - \bar{x}_{st})^2 + \frac{1}{4} (x_i - \bar{x}_{st})^4 + \frac{D}{8d} \sum_i (x_{i+1} - x_i)^2 \right) \right\},$$  \hfill (V.33)

which, because of the quartic term, no longer belongs to the class of infinitely divisible laws (see also Eq. (III.42)). On the other hand, in two dimensions the diffusion term is of order $O(\epsilon^{1/2})$ compared to the dominant chemical terms and it may become comparable to higher-order chemical terms, if any. For instance if the chemical kinetics involves fifth-order nonlinearities, one would obtain a term in $u_i^5$ in Eq. (V.32) which is also of order $O(\epsilon^{1/2})$. This cannot happen for higher dimensionalities, as can be seen straightforwardly from Eq. (V.12).

It is also possible to give an approximative evaluation of the critical exponents. This can be carried out by the following simple arguments. Let us admit that near bifurcation the cell size can be as large as the correlation length $l_c$:

$$\epsilon^{-1/2} \sim l_c.$$  \hfill (V.34)

On the other hand, the correlation length diverges at the approach of the critical point ($f''_{st} = 0$) as

$$l_c \sim \delta^{-\nu}; \quad \delta = -f'_s.$$  \hfill (V.35)
(V.34) and (V.35) lead to the following relation between the cell size and the distance $\delta$ from the bifurcation point:

$$\delta \sim e^{1/vd}.$$  (V.36)

Now as one can see from (V.31) near the bifurcation point the exponent $a$ must be equal to $\frac{3}{2}$ and $\delta \sim \delta_1 e^{1/2}$, whence

$$vd = 2.$$  (V.37)

This gives the exact Ising exponent $\nu$ in two and four dimensions. In general, one must expect corrections to (V.37) since the increase of the effective correlation at the approach of the bifurcation point may be less than that predicted by the correlation length $l_c$. In fact, as we already pointed out in the previous section, a description in terms of enlarged cells is only possible if the diffusional equilibrium is reached inside each cell. Now, for a given distance from the critical point, the diffusional equilibrium is expected to extend over some length $l_D$ which takes into account not only the relative time scale of diffusion and of chemical processes, but also the nonlinear coupling which may arise between them near the bifurcation point. This length $l_D$ can therefore be considered as an "effective correlation length" which may not necessarily be equal to $l_c$. Whether one can go further along this line is not clear at present.

Let us now consider the more general case of degenerate bifurcations in systems with nonlinearities of order higher than three. Let $k$ be the lowest nonvanishing order of the derivative of the rate function (see Eq. (111.40)). The balance between different terms in (V.12) leads to the following relation between the exponent $a$, the critical dimensionality $d_c$ and the degree of nonlinearity $k$:

$$-1 + 2a = (k - 1)(1 - a) = \frac{2}{d_c}.$$  (V.38)

From the first relation we obtain:

$$a = \frac{k}{k + 1},$$  (V.39)

hence

$$d_c = 2 \frac{k + 1}{k - 1}.$$  (V.40)

For $k = 3$ (cusp bifurcation) we find $d_c = 4$ as expected. Of interest is the case $k = 5$, corresponding to the confluence of two successive bifurcation points in a system where the nonlinearity is of fifth degree. Such degenerate cases are analogs of "tricritical" points familiar from equilibrium critical phenomena. From (V.39) and (V.40) we obtain

$$a = \frac{5}{8}, \quad d_c = 3.$$  (V.41)
More generally as \( k \) becomes very large ("infinite critical" point) one has the limiting behaviour

\[
a \to 1, \quad d_c \to 2. \tag{V.42}
\]

VI. Conclusions

In this paper we have developed a workable approach to the study of stochastic processes in nonequilibrium systems, which is independent of the number of variables involved and of special conditions like, for instance, detailed balance. The starting point is the assumption of a Markovian jump process in an appropriate phase space. The details of the mechanism responsible for the various dynamical processes appear explicitly in the transition probabilities. Because of the local character of these processes, the transition probabilities were taken to be extensive. On the other hand, no assumption concerning the validity of the phenomenological rate equations is needed; the only macroscopic element involved is the use of the rate constants of chemical kinetics in the transition probabilities.

In the case of spatially homogeneous systems, the method allows us to study the asymptotic behaviour of the probability distribution before, near and at a bifurcation point. In particular, the analyticity of the generating function near \( s = 1 \) leads to a straightforward evaluation of the spectrum of the kinetic operator. In all these situations, the asymptotic behaviour turns out to be equivalent to that obtained from the solution of a Langevin or Fokker-Planck equation with process-independent noise.

In addition to this asymptotic equivalence between a jump process and a diffusion process [17, 22], one should also notice the deviation from the central limit theorem arising at the bifurcation point. The probability function then takes a form which does not belong to the class of infinitely divisible distributions.

Two questions remain open as regards the application of our method to uniform systems: the initial value problem and the occurrence of multiple steady states. In the first case, the difficulties are mainly technical and are of the same kind as those pointed out recently by several authors [30, 36, 37, 51]. The problem of multiple steady states is deeper for it raises the question of the very applicability of the method and the possibility of defining some equivalent process with continuous realisations. It is clear that in this case a diffusion process with process-independent noise cannot be expected. Indeed, the noise amplitude \( Q \) (see Eq. (III.34)) has to be evaluated along the deterministic path and it has therefore a different value for each of the coexisting macroscopic states. However it comes as a surprise that even a diffusion process with process-dependent noise does not describe exactly the asymptotic properties of the master equation [22, 53]. This suggests that in the region of multiple steady states, the continuous process resulting as an asymptotic limit of the Master Equation might be non-Markovian. Such non-Markovian theories are indeed being currently applied in the modelling of spinodal decomposition and nucleation phenomena [39].
The extension of the method in the presence of inhomogeneous fluctuations requires an additional Ansatz, whose status has not been clearly assessed so far, namely the possibility of using the inverse of the volume of the spatial cell as a small parameter. In addition to the intuitive arguments given in Section II to support this hypothesis near a bifurcation point, computer simulations carried out recently appear to confirm the qualitative predictions of the previous sections where this hypothesis has been used \[49, 50\]: Far from bifurcation one finds a multi-Gaussian distribution. Near a bifurcation point, however, this is no longer the case; in one dimension the correlation apparently remains integrable \[49\], whereas in two dimensions abnormal behaviour of the correlation functions has been observed \[50\]. So far the computer simulations do not provide sufficient data allowing us to be more specific concerning this last point.

The appearance of a critical dimensionality and of a distribution function displaying a nonnegligible quartic term at, as well as close to the bifurcation point reflects the similarities between the Master Equation approach to nonequilibrium bifurcations and the theory of critical phenomena. Despite such analogies however, one should be fully aware of the basic differences between the types of transition as regards the mechanism responsible for the generation of critical behaviour \[40\].

We have already mentioned that the problem of multiple steady states in homogeneous systems remains practically open. A fortiori, in the presence of inhomogeneous fluctuations and nucleation phenomena the behaviour remains unknown.

Throughout this paper, we have presented the method in the context of chemical systems. However, a similar approach can be applied to hydrodynamic systems \[42–45\], spin systems \[46\] and other systems involving strongly interacting macroscopic degrees of freedom.

**ACKNOWLEDGMENTS**

We would like to thank Professors I. Prigogine, B. Schieve, C. W. Gardiner and Drs. J. S. Turner, P. Hanusse, P. Borckmans and J. Houard for fruitful discussions. This work was partially supported by the Belgian Government: Actions de Recherche Concert es, Convention n° 76/81.II.3.

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