

An Asymptotic Expansion of the Nonlinear Master Equation

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Recently, a nonlinear master equation has been suggested to account for the effect of diffusion in the fluctuations of nonlinear systems away from equilibrium. An asymptotic expansion of the solutions of this master equation in the inverse of the diffusion constant is presented. The applicability of the method is illustrated with several examples of model chemical reactions.

KEY WORDS: Fluctuations; master equation; asymptotic expansion; nonlinear systems.

1. INTRODUCTION

Recently, Prigogine and Nicolis^(1,2) stressed the necessity of a local description of fluctuations in nonlinear systems away from equilibrium. A macroscopic system is considered as a set of cells whose size is of the order of the mean free path and which communicate between themselves via a transport of matter. The variables of the stochastic description are the numbers of particles in the various cells. This leads to a multivariable probability and the master equation that governs its evolution consists of two parts^(3,4): one that takes into account the change due to chemical reactions in each single cell and which is described by the birth and death formalism, and a second one that represents the diffusion between the different cells.

Since this multivariate master equation is not easy to handle, a simplified version has been worked out, which can be regarded as a "mean-field" theory of fluctuations. In this approach a subvolume is considered whose size corresponds to the correlation length of the fluctuations and can thus be regarded to be statistically independent of the rest of the system. The

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stochastic variable is the number of particles in this subvolume,² which is coupled via diffusion to its environment. In the case of a macroscopically homogeneous system the latter is taken into account in the mean, and this leads to a nonlinear master equation.^(1,2) This formalism was used recently by Nicolis *et al.*⁽⁶⁾ to study the onset of instabilities. Even in this simplified version the calculation of the exact solution of that master equation is only rarely possible.

For linear master equations different expansions—e.g., in the inverse of the system size, which is considered to be large⁽⁶⁾ have been proposed to obtain approximate solutions. However, these expansions in a parameter only implicitly contained in the master equation finally imply a truncation of the hierarchy of moments which is not justified if the moments are of comparable importance. This is the case for a multimodal distribution or for systems in the vicinity of a transition. In these situations therefore such an expansion becomes inadequate. The nonlinear master equation, on the other hand, contains explicitly a parameter, the diffusion coefficient, which can serve as an expansion parameter: It shows a resemblance with the equations encountered in kinetic theory and therefore one could seek for asymptotic solutions of a kind similar to the Chapman–Enskog solution of the Boltzmann equation,⁽⁷⁾ namely an asymptotic expansion in the inverse of the diffusion constant. As is well known, the Chapman–Enskog expansion is based on the presence of processes evolving according to two different time scales in the Boltzmann equation: one associated with the free motion of the particles, and a second associated with collisions.

Now this is exactly what happens in the nonlinear master equation of the mean-field theory—and in the multivariate description as well—except that the role of the reaction and diffusion contributions are somewhat the “inverse” of the collision and free-particle contributions in the Boltzmann equation: Indeed, in our case the reactive collisions tend to destroy the Poisson distribution—the analog of local equilibrium in kinetic theory—whereas diffusion tends to reestablish this distribution. This suggests the existence of an expansion, provided the diffusion is much more rapid than the macroscopic evolution due to chemical reactions, which would thus furnish a systematic scheme providing approximate solutions.

In Section 2 we will present the general formulation of such an expansion, namely an asymptotic expansion in the inverse of the diffusion parameter. Since the range of validity of this expansion cannot be established in general—a situation often encountered in dealing with asymptotic expansions—its application will be considered in several particular cases. Section 3 deals with systems in which only the elementary reaction steps ± 1 are possible.

² It should be noticed that there is of course no relation between the size of the above-mentioned cells and that of this subvolume.

In this case the principle of detailed balance is obeyed, so that the exact stationary solution can be found by a recurrence formula. In Section 4 we will deal with an example where the exact stationary solution is known but the principle of detailed balance does not hold. In Section 5 we will study the time-dependent solution for a linear and therefore exactly soluble system.

Whereas in this paper examples are given only to illustrate the method of the asymptotic expansion, a subsequent paper will deal with the stability properties of the solutions of the nonlinear master equation. In particular, the problem of chemical instabilities far from equilibrium will be studied in detail.

2. AN ITERATION PROCEDURE FOR ASYMPTOTIC SOLUTIONS OF THE NONLINEAR MASTER EQUATION

The probability $P(x, \tau)$ of finding x particles in the subvolume ΔV of the overall reaction volume obeys, if the system remains macroscopically homogeneous, the following master equation⁽²⁾:

$$\begin{aligned} dP/d\tau = R_{\text{ch}} + \mathcal{D}\langle x \rangle [P(x-1, \tau) - P(x, \tau)] \\ + \mathcal{D}[(x+1)P(x+1, \tau) - xP(x, \tau)] \end{aligned} \quad (1)$$

where R_{ch} describes the change of $P(x, \tau)$ due to the chemical reactions in ΔV and \mathcal{D} is the rate of exchange of matter between ΔV and $V - \Delta V$.

Obviously P depends on \mathcal{D} and, as is well known,⁽²⁾ as \mathcal{D} increases, P approaches a Poisson distribution.

Let t_{ch} be the characteristic time scale of (macroscopic) evolution due to the chemical reactions and t_r be that of the diffusion (cf. the discussion in Section 1). If

$$t_{\text{ch}}\mathcal{D} \sim t_{\text{ch}}/t_r \gg 1$$

we can introduce the dimensionless smallness parameter $\epsilon = 1/t_{\text{ch}}\mathcal{D}$. Rescaling the time $t = \tau/t_{\text{ch}}$, we obtain from (1)

$$\begin{aligned} \frac{dP}{dt} = R_{\text{ch}} + \frac{1}{\epsilon} \{ \langle x \rangle [P(x-1, t) - P(x, t)] \\ + (x+1)P(x+1, t) - xP(x, t) \} \end{aligned} \quad (2)$$

From (2) it is suggestive to try to represent its solution as an asymptotic expansion with respect to ϵ :

$$P(x, t, \epsilon) = P^{(0)}(x, t) + \epsilon P^{(1)}(x, t) + \dots \quad (3)$$

and similarly

$$\langle x^n \rangle = \langle x^n \rangle^{(0)} + \epsilon \langle x^n \rangle^{(1)} + \dots \quad (4)$$

Let us for the moment assume that such an expansion is meaningful and investigate how $P^{(n)}$ can be calculated. We will show that this can be done by an iteration and that $P^{(0)}$ is a Poisson distribution. In other words (3) can be interpreted as a perturbation expansion around the Poisson distribution.

It is convenient to switch to the generating function representation:

$$F(s, t) = \sum_{x=0}^{\infty} s^x P(x, t) \quad (5)$$

$$F(s, t) = F^{(0)}(s, t) + \epsilon F^{(1)}(s, t) + \dots \quad (6)$$

Furthermore, it is clear that the norm of $P(x, t)$ is independent of ϵ , i.e., $\sum_x P(x, t) = 1$ for all ϵ , so that

$$\sum_x P^{(0)}(x, t) = 1, \quad \sum_x P^{(n)}(x, t) = 0 \quad \text{for } n \geq 1 \quad (7)$$

These relations yield for the generating function

$$F^{(0)}(s, t)|_{s=1} = 1, \quad F^{(n)}(s, t)|_{s=1} = 0, \quad n \geq 1 \quad (8)$$

From (2) we can derive the following evolution equation for the generating function:

$$\partial_t F(s, t) = \tilde{R}_{\text{ch}} F(s, t) + (1/\epsilon)(s-1)[\langle x \rangle - \partial_s] F(s, t) \quad (9)$$

In the range of validity of the asymptotic expansion, Eqs. (2) and (9) have to hold for any order in ϵ . Since the "chemical operator" is independent of \mathcal{Q} , we find for the dominant order ϵ^{-1}

$$[\langle x \rangle^{(0)} - \partial_s] F^{(0)}(s, t) = 0 \quad (10)$$

For convenience we will present all calculations in the generating function representation, but of course all steps can also be performed without difficulty in the probability distribution representation.

The only solution of (10) is the Poisson distribution:

$$F^{(0)}(s, t) = \exp[\langle x \rangle_i^{(0)}(s-1)]$$

or

$$P^{(0)}(x, t) = [\exp(-\langle x \rangle_i^{(0)})] \langle x \rangle_i^{(0)x} / x! \quad (11)$$

Obviously $\langle x \rangle_i^{(0)}$ still has to be determined. This can be done by considering the next order, i.e., ϵ^0 :

$$\partial_t F^{(0)}(s, t) = \tilde{R}_{\text{ch}} F^{(0)} + (s-1)[\langle x \rangle^{(0)} F^{(1)} + \langle x \rangle^{(1)} F^{(0)} - \partial_s F^{(1)}] \quad (12)$$

Taking derivatives of both sides with respect to s and setting $s = 1$, we obtain

$$\langle \dot{x} \rangle_i^{(0)} = \partial_t \partial_s F^{(0)}|_{s=1} = \partial_s \tilde{R}_{\text{ch}} F^{(0)}|_{s=1} \quad (13)$$

It is well known⁽²⁾ that for a Poisson distribution the evolution equation for the mean is identical to the macroscopic kinetic equation. Therefore the macroscopic kinetic evolution determines $\langle x \rangle^{(0)}$ —and thus also $P^{(0)}$ —completely.

Note that this implies multiple stationary solutions for $P^{(0)}$ and for $P(x)$, if the macroscopic kinetic equation admits multiple steady states, provided the asymptotic expansion remains valid. We will now formulate the iteration procedure to calculate the $(m + 1)$ th correction to $F^{(0)}$.

Let us assume that $F^{(n)}(s, t)$ is known for $n \leq m$. For the m th order, Eq. (9) yields

$$\begin{aligned} \partial_s F^{(m)}(s, t) = & \tilde{R}_{\text{ch}} F^{(m)} + (s - 1)[\langle x \rangle^{(0)} F^{(m+1)}(s, t) \\ & + \langle x \rangle^{(1)} F^{(m)} + \langle x \rangle^{(2)} F^{(m-1)} + \dots + \langle x \rangle^{(m+1)} F^{(0)}] \\ & - (s - 1) \partial_s F^{(m+1)} \end{aligned} \tag{14}$$

Rearranging terms, we find

$$\partial_s F^{(m+1)} - \langle x \rangle^{(0)} F^{(m+1)} = \varphi^{(m)}(F^{(0)}, \dots, F^{(m)}, \langle x \rangle^{(0)}, \dots, \langle x \rangle^{(m+1)}) \tag{15}$$

The solution of this equation is

$$F^{(m+1)}(s, t) = \{\exp[\langle x \rangle^{(0)}(s - 1)]\} \psi^{(m)}(s, t) \tag{16}$$

where $\psi^{(m)}(s, t)$ denotes

$$\begin{aligned} \psi^{(m)}(s, t) = & \int_1^s d\xi \{\exp[-\langle x \rangle^{(0)}(\xi - 1)]\} \\ & \times \varphi^{(m)}(F^{(0)}(\xi, t), \dots, F^{(m)}(\xi, t), \langle x \rangle^{(0)}, \dots, \langle x \rangle^{(m+1)}) \end{aligned} \tag{17}$$

As was the case for the zeroth order, $\langle x \rangle^{(m+1)}$ is yet undetermined.

By taking derivatives of both sides of the equation for $F^{(m+1)}(s, t)$ and putting $s = 1$, we find, however,

$$\partial_i \langle x \rangle^{(m+1)} = \partial_s \tilde{R}_{\text{ch}} F^{(m+1)}|_{s=1} \tag{18}$$

The right-hand side will be a function of $\{\langle x^i \rangle^{(m+1)}\}$, where i depends on the order of the reactions. For any i , $\langle x^i \rangle^{(m+1)}$ can be expressed as a function of $\{\langle x \rangle^{(0)}, \dots, \langle x \rangle^{(m+1)}\}$ via equation (16), so that we finally find³

$$\partial_i \langle x \rangle^{(m+1)} = \Phi(\langle x \rangle^{(0)}, \dots, \langle x \rangle^{(m+1)}) \tag{19}$$

This enables us to determine $\langle x \rangle_i^{(m+1)}$ and thus complete the computation of the $(m + 1)$ th correction.

In conclusion, there exists an iteration procedure to calculate as many corrections to the Poisson distribution as desired. It is the purpose of the

³ Note that (19) is in general different from the macroscopic equation since $P^{(m+1)}$ will in general not be a Poisson distribution.

subsequent sections to test the validity as well as the kind of information obtained from this method on representative, simple examples.

3. MODELS WITH ELEMENTARY REACTION STEPS ± 1

In this section we consider a chemical system in which only reactions of the type



take place.

The contribution from each reaction path ρ to the birth rate $B(x)$ and the death rate $D(x)$ is

$$B_\rho(x-1) = b_\rho(1/\nu_\rho!)(x-1)\cdots(x-\nu_\rho) \quad \text{for } \nu_\rho \geq 1 \quad (21)$$

$$B_\rho(x-1) = b_\rho \quad \text{for } \nu_\rho = 0$$

$$D_\rho(x) = d_\rho(1/\nu_\rho!)(x-1)\cdots(x-\nu_\rho) \quad (22)$$

The stationary solution can be found by a recurrence formula, which has already been applied by other authors in the absence of diffusion,⁽⁸⁻¹⁰⁾

$$P_{\text{st}}(x) = \prod_{j=1}^x \frac{B(j-1) + \epsilon^{-1}\langle x \rangle}{D(j) + \epsilon^{-1}j} P_{\text{st}}(0) \quad (23)$$

where $B(i) = \sum_\rho B_\rho(i)$ and $D(i) = \sum_\rho D_\rho(i)$. Since $D(x)$ can be written in the form $D(x) = x\tilde{D}(x)$, Eq. (23) yields

$$P_{\text{st}}(x) = \frac{1}{x!} \prod_{j=1}^x \frac{B(j-1) + \epsilon^{-1}\langle x \rangle}{\tilde{D}(j) + \epsilon^{-1}} P_{\text{st}}(0) \quad (24)$$

It can be shown that there exists a $K < \infty$ such that

$$\frac{B(j-1) + \epsilon^{-1}\langle x \rangle}{\tilde{D}(j) + \epsilon^{-1}} \leq K \quad \text{for all } j \text{ and } \epsilon \quad (25)$$

From this it follows that $\sum_x P_{\text{st}}(x) < \infty$, i.e., $P_{\text{st}}(x)$ is normalizable. The condition $\sum_x P_{\text{st}}(x) = 1$ determines $P_{\text{st}}(0)$.

From (25) it also follows that there exists an M (independent of ϵ , i.e., \mathcal{D}) such that

$$P[x \geq L] < C \exp(-L) \quad \text{for } L \geq M \quad (26)$$

This property should be expected for a realistic model, since the number of particles X that can be found in the subvolume ΔV possesses of course a finite upper bound G . Since by construction of the master equation, i.e., by the idealizations made in deriving it, this upper bound is discarded, the probability for a very large number of particles (with respect to G) should

decrease sufficiently rapidly for the description to be considered sufficiently realistic. This also ensures the existence of all moments $\langle x^n \rangle$.

Let us now consider an $L \geq M$ and define a probability $P^L(x)$ by

$$\begin{aligned} \tilde{P}^L(x) &= P_{st}(x) & \text{if } x \leq L \\ &= 0 & \text{if } x > L \end{aligned} \tag{27}$$

and $P^L(x) = (1/\sigma)\tilde{P}^L(x)$, with $\sigma = \sum \tilde{P}^L(x)$.

It is important to notice that by choosing L sufficiently large, $P^L(x)$ will become as close as desired to $P_{st}(x)$,

$$\sup_{\mathbb{R}^+} |P^L(x) - P_{st}(x)| \leq C \exp(-L) \tag{28}$$

i.e., the “distance” between the probabilities will decrease exponentially with L . So $P^L(x)$ can be made indistinguishable from the rigorous solutions $P_{st}(x)$ for all practical purposes.

For $x \leq L$, $\hat{P}^L(x) = P^L(x)/P^L(0)$,

$$\hat{P}^L(x) = \frac{1}{x!} \prod_{j=1}^x \frac{\epsilon B(j-1) + \langle x \rangle}{\epsilon \tilde{D}(j) + 1} \tag{29}$$

If the dominant term of $\tilde{D}(x)$ is of the power n ($n = \max\{\nu_\rho\}$), then the denominator in the product of (29) can be developed as

$$1/[1 + \epsilon \tilde{D}(j)] = 1 - \epsilon \tilde{D}(j) + \epsilon^2 \tilde{D}(j)^2 + \dots \tag{30}$$

provided $\epsilon < \alpha L^{-n}$.

This means that $P^L(x)$ is expandable in a convergent series $P^L(x) = P_{(0)}^L(x) + \epsilon P_{(1)}^L(x) + \epsilon^2 P_{(2)}^L(x) + \dots$ with the radius of convergence $r = \alpha L^{-n}$. This expansion is of course only valid if it is compatible with the existence of finite $\langle x \rangle^{(n)}$ [see (40)]. If we want to increase the precision with which $P^L(x)$ approximates $P_{st}(x)$ by, say, a factor ten, we have to choose $L' = L + \ln 10$. Since $L \gg 1$, this has almost no influence on the radius of convergence.

This means that for $\epsilon < r \sim L^{-n}$ the ϵ expansion converges to a function $P^L(x)$ which is “infinitesimally” close to the rigorous solution $P_{st}(x)$ and is therefore an asymptotic solution of the nonlinear master equation.

As a concrete example, let us consider the following model^(10,11):



We put $a = k_1 A/k_2$, $b = k_4 B/k_2$, $k = k_3/k_2$, and $1/\epsilon = \mathcal{D}/k_2$. Since chemical kinetics is formulated for intensive quantities, such as concentration, it is

clear that in the particle number space in which we work $a = O(N)$, $b = O(N^3)$, $k = O(N^2)$, and $1/\epsilon = O(N^2)\mathcal{O}$, where N is the total number of particles in the subvolume, $N = \rho \Delta V \sim R^3$, where R is the radius of the subvolume.

We find from (33)

$$\begin{aligned} P_{\text{st}}(x)[x(x-1)(x-2) + kx + \epsilon^{-1}x] \\ = [a(x-1)(x-2) + b + \epsilon^{-1}\langle x \rangle]P_{\text{st}}(x-1) \end{aligned} \quad (32)$$

In terms of the generating function $F(s)$ this relation yields

$$s^2 \frac{d^3 F}{ds^3} - as^2 \frac{d^2 F}{ds^2} + k \frac{dF}{ds} - bF + \epsilon^{-1} \left[\frac{dF}{ds} - \langle x \rangle F \right] = 0 \quad (33)$$

or

$$R_{\text{ch}}F(s) + \epsilon^{-1}[(dF/ds) - \langle x \rangle F] = 0$$

For the zeroth order $F^{(0)}(s)$ we find

$$F^{(0)}(s) = \exp[\langle x \rangle_{(0)}(s-1)] \quad (34)$$

where $\langle x \rangle_{(0)}$ is a solution of

$$\langle x \rangle_{(0)}^3 - a\langle x \rangle_{(0)}^2 + k\langle x \rangle_{(0)} - b = 0 \quad (35)$$

i.e., a stationary solution of the kinetic equation. It is well known that there exists a domain in the parameter space (a, b) such that (35) admits three solutions, one unstable and two stable ones. This has the consequence that we find three stationary solutions of the nonlinear master equation.

We now proceed to calculate the first correction $F^{(1)}(s)$. We have

$$dF^{(1)}/ds - \langle x \rangle^{(0)}F^{(1)} = \langle x \rangle^{(1)}F^{(0)} - R_{\text{ch}}F^{(0)} \quad (36)$$

This has the form of Eq. (15). The solution $F^{(1)}(s)$ is [see (16) and (17)]

$$F^{(1)}(s) = \{\exp[\langle x \rangle_{(0)}(s-1)]\}\psi^{(1)}(s, t) \quad (37)$$

where

$$\begin{aligned} \psi^{(1)}(s, t) = \langle x \rangle_{(1)}(s-1) - \frac{1}{3}\langle x \rangle_{(0)}^3(s^3-1) \\ + \frac{1}{3}a\langle x \rangle_{(0)}^2(s^3-1) - k\langle x \rangle_{(0)}(s-1) + b(s-1) \end{aligned} \quad (38)$$

It is easy to verify that $(dF^{(1)}/ds)|_{s=1} = \langle x \rangle_{(1)}$. To determine $\langle x \rangle_{(1)}$ we consider the equation

$$R_{\text{ch}}F^{(1)} = \langle x \rangle^{(0)}F^{(2)} + \langle x \rangle^{(1)}F^{(1)} + \langle x \rangle^{(2)}F^{(0)} - dF^{(2)}/ds \quad (39)$$

Putting $s = 1$, we obtain

$$R_{\text{ch}}F^{(1)}|_{s=1} = 0$$

This yields by straightforward calculation

$$\langle x \rangle^{(1)} = \frac{-6k\langle x \rangle_{(0)}^2 + \langle x \rangle_{(0)}[6b + 2ak - 2k] - 2b(a - 1)}{3\langle x \rangle_{(0)}^2 - 2a\langle x \rangle_{(0)} + k} \tag{40}$$

This first-order correction tends to infinity if the denominator tends to zero, which happens for values of parameters a and b such that Eq. (35) has a real double root, i.e., at the macroscopic transition points. Due to the hard transition at these points $\langle x \rangle_{(0)}$ changes discontinuously, a finite $\langle x \rangle_{(1)}$ no longer exists, and our expansion breaks down.

Below we list the values of $\langle \bar{x} \rangle_{(1)} = \epsilon^{-1}(\langle x \rangle - \langle x \rangle_{(0)})$, obtained by a numerical evaluation of the exact stationary probability (33). Choosing $a = 200$, $b = 110,000$, and $k = 10,000$, we find $\langle x \rangle_{(0)} = 15.35168$.

ϵ	10^{-4}	10^{-5}	10^{-6}	10^{-7}
$\langle \bar{x} \rangle_{(1)}$	2150	2809	2909	2914

From (40) we obtain for the first correction

$$\langle x \rangle_{(1)} = 2915.1$$

We see that as ϵ decreases, $\langle \bar{x} \rangle_{(1)}$ approaches the theoretical value $\langle x \rangle_{(1)}$, and that the difference between these two values behaves like a term of the order of ϵ .

Since for a Poissonian $\langle (\delta x)^2 \rangle \equiv \langle x^2 \rangle - \langle x \rangle^2 = \langle x \rangle$, we give the expression for $\langle (\delta x)^2 \rangle$ up to first order in ϵ to show in a concise way how the first correction affects the Poisson distribution:

$$\langle (\delta x)^2 \rangle = \langle x \rangle_{(0)} + \epsilon[\langle x \rangle_{(1)} - 2\langle x \rangle_{(0)}^2 + 2a\langle x \rangle_{(0)}^2]$$

4. A MODEL WITH ELEMENTARY REACTION STEPS ± 1 AND ± 2

In this section we will consider the autocatalytic model



The stationary solution cannot be found by a recurrence formula in this case.

The equation for the generating function $F(s)$ is, in the stationary case,

$$\left[\frac{k_2}{2}(s + 1) \frac{d^2}{ds^2} - k_1 A s \frac{d}{ds} \right] F = \mathcal{D} \left[\langle x \rangle - \frac{d}{ds} \right] F \tag{42}$$

or, with $\epsilon^{-1} = \mathcal{D}/k_2$,

$$\left(\frac{s+1}{2} \frac{d^2}{ds^2} - \frac{k_1 A}{k_2} s \frac{d}{ds} \right) F = \epsilon^{-1} \left(\langle x \rangle - \frac{d}{ds} \right) F \quad (43)$$

where $k_1 A/k_2 = O(N)$ and $\epsilon^{-1} = O(N)\mathcal{D}$.

According to (11), we obtain for $F^{(0)}(s)$

$$F^{(0)}(s) = \exp[\langle x \rangle^{(0)}(s-1)] \quad (44)$$

with

$$\langle x \rangle^{(0)} = 0 \quad \text{or} \quad \langle x \rangle^{(0)} = k_1 A/k_2 \quad (45)$$

In the following we will consider only the nontrivial case $\langle x \rangle^{(0)} = k_1 A/k_2$.

Formulas (16)–(18) yield

$$F^{(1)}(s) = \{ \exp[\langle x \rangle^{(0)}(s-1)] \} \\ \times \left[\frac{(s-1)^2}{2} \left(\frac{k_1 A}{k_2} \langle x \rangle^{(0)} - \frac{1}{2} \langle x \rangle_{(0)}^2 \right) + \langle x \rangle^{(1)}(s-1) \right] \quad (46)$$

where

$$\langle x \rangle^{(1)} = -k_1 A/2k_2 \quad (47)$$

So we obtain

$$\langle x \rangle = \frac{k_1 A}{k_2} - \epsilon \frac{k_1 A}{2k_2} + O(\epsilon^2) \quad (48)$$

On the other hand, it is possible to calculate the exact stationary solution for the generating function (see Ref. 2, Appendix A).

Transforming to the new variable

$$z = (s+1)(2k_1 A)/k_2 \quad (49)$$

we obtain for (42)

$$z \frac{d^2 F}{dz^2} + \left(\frac{2(\mathcal{D} + k_1 A)}{k_2} - z \right) \frac{dF}{dz} - \frac{\mathcal{D} \langle x \rangle}{k_1 A} F = 0 \quad (50)$$

with the boundary conditions

$$F(4k_1 A/k_2) = 1, \quad F(0) \text{ finite} \quad (51)$$

The solution of Eq. (50) under the conditions (51) is the confluent hypergeometric function ${}_1\psi_1$:

$$F(z) = {}_1\psi_1(a, b, z) / {}_1\psi_1(a, b, 4k_1 A/k_2) \quad (52)$$

where

$$a = \epsilon^{-1} k_2 \langle x \rangle / k_1 A, \quad b = 2(\epsilon^{-1} + k_1 A/k_2) \quad (53)$$

Using the well-known Laplace integral representation of the confluent hypergeometric function (see Ref. 12), we find

$${}_1\psi_1(a, b, z) = \frac{\Gamma(b)}{\Gamma(a)\Gamma(b-a)} \int_0^1 du \varphi(u) \exp[\epsilon^{-1}f(u)] \tag{54}$$

with

$$\varphi(u) = u^{-1}e^{zu}(1-u)^{(2k_1A/k_2-1)} \tag{55}$$

and

$$f(u) = \langle x \rangle \frac{k_2}{k_1A} \ln u + \left(2 - \frac{k_2\langle x \rangle}{k_1A} \right) \ln(1-u) \tag{56}$$

According to a theorem about asymptotic expansions,^(13,14) the integral (54) admits such an asymptotic representation if the function $f(u)$ assumes its maximum in the interval $(0, 1)$.

This is indeed the case, as is easily seen, if $k_1A > k_2$, which of course holds, since $k_1A/k_2 = O(N)$. Using these results, it can be shown by tedious and rather lengthy calculations that

$$F(s) = e^{(s-1)\langle x \rangle} \left[1 + \frac{\epsilon}{2} (s-1)^2 \left(\frac{k_1A}{k_2} \langle x \rangle - \frac{1}{2} \langle x \rangle^2 \right) \right] + O(\epsilon^2) \tag{57}$$

This implies that the mean value $\langle x \rangle$ can also be represented as

$$\langle x \rangle = \langle \tilde{x} \rangle_{(0)} + \epsilon \langle \tilde{x} \rangle_{(1)} + O(\epsilon^2)$$

Indeed, Eq. (43) yields for $s = 1$

$$\langle x \rangle^2 + \epsilon \left[\frac{k_1A}{k_2} \langle x \rangle - \frac{1}{2} \langle x \rangle^2 \right] - \frac{k_1A}{k_2} \langle x \rangle + O(\epsilon^2) = 0 \tag{58}$$

In addition to the trivial case $\langle x \rangle = 0$ we obtain

$$\begin{aligned} \langle x \rangle &= \left(\frac{k_1A}{k_2} - \epsilon \frac{k_1A}{k_2} \right) \left(1 - \frac{\epsilon}{2} \right)^{-1} + O(\epsilon^2) \\ &= \left(\frac{k_1A}{k_2} - \epsilon \frac{k_1A}{k_2} \right) \left(1 + \frac{\epsilon}{2} \right) + O(\epsilon^2) \quad \text{if } \mathcal{D} > k_2/2 \\ &= \frac{k_1A}{k_2} - \epsilon \frac{k_1A}{2k_2} + O(\epsilon^2) \end{aligned} \tag{59}$$

So we finally obtain as an asymptotic expansion for $F(s)$

$$\begin{aligned} F(s) &= \left[\exp \frac{(s-1)k_1A}{k_2} \right] \\ &\times \left\{ 1 + \epsilon \left[\frac{(s-1)^2}{4} \left(\frac{k_1A}{k_2} \right)^2 + (s-1) \left(-\frac{k_1A}{2k_2} \right) \right] \right\} + O(\epsilon^2) \end{aligned} \tag{60}$$

This coincides with the expansion above calculated, Eqs. (44) and (46):

$$F(s) = F^{(0)}(s) + \epsilon F^{(1)} + O(\epsilon^2)$$

and thus clearly shows that the ϵ expansion given in Section 2 represents in this example an asymptotic expansion whose properties are well established, even if it is not a convergent expansion in the ordinary sense.

As in Section 3, let us calculate the first correction to the variance:

$$\langle(\delta x)^2\rangle = \langle x \rangle_{(0)} + \frac{1}{2}\epsilon[\langle x \rangle_{(0)}^2 - \langle x \rangle_{(0)}]$$

5. THE TIME-DEPENDENT SOLUTION FOR A LINEAR MODEL

In order to discuss the applicability of the ϵ expansion for the time-dependent solution, we consider the linear chemical reaction



The master equation for (61) is

$$\begin{aligned} dP/d\tau &= k_1AP(x-1, \tau) - k_1AP(x, \tau) + k_2(x+1)P(x+1, \tau) - k_2xP(x, \tau) \\ &+ \mathcal{D}\langle x \rangle [P(x-1, \tau) - P(x, \tau)] \\ &+ \mathcal{D}[(x+1)P(x+1, \tau) - xP(x, \tau)] \end{aligned} \quad (62)$$

Due to the linearity of the system, the evolution of the mean obeys the equation

$$\langle \dot{x} \rangle = k_1A - k_2\langle x \rangle \quad (63)$$

This relation is identical to the macroscopic kinetic equation.

We can therefore in this case identify t_{ch} with k_2^{-1} and Eq. (2) has the form

$$\begin{aligned} \frac{dP}{dt} &= \frac{k_1A}{k_2}P(x-1, t) - \frac{k_1A}{k_2}P(x, t) + (x+1)P(x+1, t) - xP(x, t) \\ &+ \epsilon^{-1}\{\langle x \rangle [P(x-1, t) - P(x, t)] + (x+1)P(x+1, t) - xP(x, t)\} \end{aligned} \quad (64)$$

The corresponding equation for the generating function is

$$\partial_t F + (s-1)(1 + \epsilon^{-1}) \partial_s F = (s-1)(\langle x \rangle / \epsilon + k_1A/k_2)F \quad (65)$$

The general solution of Eq. (65) is easily calculated to be

$$F(s, t) = \exp((s - 1)\{\langle x \rangle - x_0 \exp[-(1 + \epsilon^{-1})t]\}) \times F_0((s - 1) \exp[-(1 + \epsilon^{-1})t] + 1) \quad (66)$$

where $F_0(\cdot)$ is the generating function at $t = 0$ and

$$\langle x(t) \rangle = (x_0 - k_1 A/k_2)e^{-t} + k_1 A/k_2 \quad (67)$$

Let us consider two special initial distributions:

$$P(x, 0) = \delta_{x, x_0} \quad \text{and} \quad P(x, 0) = \frac{\langle x(0) \rangle^x}{x!} \exp(-\langle x(0) \rangle)$$

In the first case (66) yields

$$F(s, t) = \exp((s - 1)\{\langle x \rangle - x_0 \exp[-(1 + \epsilon^{-1})t]\}) \times \{(s - 1) \exp[-(1 + \epsilon^{-1})t] + 1\}^{x_0} \quad (68)$$

for which obviously no expansion of the form (6) exists for $t \lesssim \epsilon$. This is in complete analogy to the "initial layer" of the kinetic theory of gases.⁽¹⁵⁾ This has to be expected since our initial distribution represents a considerable deviation from a locally Poissonian behavior.

On the other hand, our ϵ expansion was based on the fact that, due to the fast diffusion, $t_{\text{ch}} \mathcal{D} \ll 1$, the system possesses locally an almost Poissonian distribution.

It is clear therefore that only on the time scale of the chemical kinetics can the ϵ expansion be valid, i.e., after the decay of the initial condition due to the diffusion effects.

If we start with a Poisson distribution at $t = 0$, we find

$$F(s, t) = \exp((s - 1)\{\langle x \rangle - x_0 \exp[-(1 + \epsilon^{-1})t]\}) \times \exp\{(s - 1)x_0 \exp[-(1 + \epsilon^{-1})t]\} = \exp[(s - 1)\langle x \rangle] \quad (69)$$

i.e., the system remains Poissonian (because of its linearity). So all higher terms in the ϵ expansion are identically zero. This example underlines once again the importance of the two different time scales.

6. CONCLUSIONS

The foregoing examples clearly demonstrate the applicability of the asymptotic expansion of $P(x, t, \mathcal{D})$ for large \mathcal{D} around the Poissonian as well as its limitations.

This method can be efficiently used for a detailed study of the implications of the nonlinearity of the master equation in the mean-field theory of

fluctuations, and a particularly interesting application would be the analysis of instabilities. As is well known,^(1,2,5) the diffusion coefficient \mathcal{D} is inversely proportional to the correlation length l . Far from a transition point, i.e., for l small, the system is well approximated by a Poisson distribution and the equation for the temporal evolution of the mean value is the macroscopic kinetic equation. The higher order corrections in our expansion take into account the effect of the small but nonzero correlation length. If the correlation length grows, as it does when a transition point is approached,^(1,2,4,5) these corrections will become more and more important and we expect the existence of a critical l and thus a critical ϵ beyond which the expansion is no longer valid. This is clearly shown in the model of Section 3, where, due to the fact that it is a hard transition, ϵ_{crit} tends to zero as the transition point is approached. The model of Section 4 shows a soft transition and the existence of an ϵ_{crit} cannot be as easily decided. This will be discussed in a subsequent paper, where the results of a detailed analysis of instabilities will be reported.

The advantage of the ϵ expansion is that no truncation of the hierarchy of the moments is implied. It is of course appealing to try to extend this method to the multivariate case^(3,4) and work in this direction is in progress.

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