Bistable systems: Master equation versus Fokker-Planck modeling

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(Received 21 March 1983)

Relaxation and fluctuations of nonlinear macroscopic systems, which are frequently described by means of Fokker-Planck or Langevin equations, are studied on the basis of a master equation. The problem of an approximate Fokker-Planck modeling of the dynamics is investigated. A new Fokker-Planck modeling is presented which is superior to the conventional method based on the truncated Kramers-Moyal expansion. The new approach is shown to give the correct transition rates between deterministically stable states, while the conventional method overestimates these rates. An application to the Schlögl models for first- and second-order nonequilibrium phase transitions is given.

I. INTRODUCTION

Nonlinear macroscopic systems which are displaced from equilibrium or driven by external forces show a rich variety of interesting phenomena as, e.g., instabilities and metastable states. These problems have attracted considerable interest in recent years.[1-3] Most of the analysis has been based on Fokker-Planck equations or stochastically equivalent Langevin equations. On the other hand, it has been pointed out previously, in particular by van Kampen,[2] that the Fokker-Planck approach has no absolute applicability; rather it represents an approximation whose form and limits of validity should be investigated in each situation.

In this paper, we consider the dynamics of bistable systems described in terms of a master equation and study the problem of an approximate Fokker-Planck modeling of the dynamics. The same problem has been investigated previously. Van Kampen[4] has introduced the system-size expansion which reduces the master equation locally to a diffusion process. This method is systematic but it does not allow for the determination of global features, as, e.g., the decay rates of metastable states. A global Fokker-Planck description can be obtained by truncating the Kramer-Moyal expansion[5,6] of the master equation after the second term. This is, in fact, the most widely used method. A third method based on nonlinear transport theory[7] has very recently been proposed by Grabert, Hanggi, and Oppenheim.[8] In the present work we relate some more details to the new Fokker-Planck modeling and show that it yields a more faithful representation of the underlying master equation than the usual Kramers-Moyal modeling.

The paper is organized as follows. In Sec. II we review the description of bistable systems in terms of one-step Markov processes. The transition probabilities are assumed to obey the usual scaling in terms of a size parameter Ω. A nonlinear Onsager-type transport law is derived asymptotically for large Ω, and the rates for transitions between the two deterministically stable states are determined. Section III discusses various features of the new Fokker-Planck modeling.[8] In particular, we calculate the transition rates from the Fokker-Planck equation and show that they coincide with the correct rates for large Ω. On the other hand, the usual Kramers-Moyal modeling is shown to consistently overestimate these rates.

In Sec. IV we study the Fokker-Planck modeling of the Schlögl models[9] for first- and second-order nonequilibrium phase transitions. In this context, the special case of a process with an absorbing state is investigated. Finally, in Sec. V we elaborate on extensions to multistep processes and higher-dimensional state spaces and discuss limitations of a Fokker-Planck modeling of discrete processes.

II. BISTABLE ONE-STEP PROCESSES

We consider a bistable system with a discrete state space $N=0,1,2,\ldots$. The number of molecules of a chemical species, the number of photons in a lasing mode, or the number of electrons on a capacitance are examples for N. It is assumed that the system makes random transitions where N jumps by $+1$ or -1 according to the transition probabilities $W^+(N)$ and $W^-(N)$. The state then follows a Markovian process, and the probability $P_t(N)$ of finding the system at time t in the state N changes according to the master equation

$$\dot{P}_t(0)=W^-(1)P_t(1)-W^+(0)P_t(0)\ , \tag{2.1a}$$

$$\dot{P}_t(N)=W^+(N-1)P_t(N-1)+W^-(N+1)P_t(N+1) -[W^+(N)+W^-(N)]P_t(N),\quad N=1,2,\ldots . \tag{2.1b}$$

In the sequel we assume that all transition probabilities are positive, $W^+(0)>0$; $W^\pm(N)>0$, $N=1,2,\ldots$. Moreover, in terms of a size parameter Ω, the transition probabilities shall obey a scaling relation

$$W^\pm(N)=\Omega\gamma^\pm(x)\ , \tag{2.2}$$

where

$$x=\frac{N}{\Omega} \tag{2.3}$$

is an intensive variable corresponding to N.

With these assumptions the Kramers-Moyal expansion of the master equation (2.1) reads

$$\frac{\partial}{\partial t}p_t(x)=\sum_{n=1}^{\infty}\frac{1}{n!}\frac{1}{\Omega^{n-1}}\left[-\frac{\partial}{\partial x}\right]^n A_n(x)p_t(x)\ , \tag{2.4}$$

where

$$p_t(x)=\Omega P_t(N) \tag{2.5}$$

is the probability density of the intensive variable x, and the

$$A_n(x)=\gamma^+(x)+(-1)^n\gamma^-(x) \tag{2.6}$$

are the Kramers-Moyal moments. Clearly, in the limit $\Omega\to\infty$, (2.4) reduces to

$$\frac{\partial}{\partial t}p_t(x)=-\frac{\partial}{\partial x}A_1(x)p_t(x) \tag{2.7}$$

which corresponds to the deterministic evolution

$$\dot{x}=A_1(x)=\gamma^+(x)-\gamma^-(x)\ . \tag{2.8}$$

The stationary probability $\bar{P}(N)$ of the master equation (2.1) satisfies the condition for detailed balancing

$$W^+(N)\bar{P}(N)=W^-(N+1)\bar{P}(N+1)\ . \tag{2.9}$$

This yields

$$\begin{aligned}\bar{P}(N)&=\bar{P}(0)\prod_{M=0}^{N-1}\frac{W^+(M)}{W^-(M+1)}\\&=\bar{P}(0)\exp\left[\sum_{M=0}^{N-1}\ln\frac{W^+(M)}{W^-(M+1)}\right]\ .\end{aligned} \tag{2.10}$$

By virtue of (2.2) and (2.10), the stationary probability of x has the asymptotic form

$$\bar{p}(x)=Z^{-1}\exp\left[-\Omega\left[\phi_0(x)+\frac{1}{\Omega}\phi_1(x)\right]\right]\ , \tag{2.11}$$

where Z denotes the normalization,

$$\phi_0(x)=-\int_{x_0}^{x}dy\ln\frac{\gamma^+(y)}{\gamma^-(y)} \tag{2.12}$$

is a potential possessing extrema at the steady states of the deterministic evolution law (2.8), and where[10]

$$\phi_1(x)=-\tfrac{1}{2}\ln\frac{\gamma^+(x_0)\gamma^-(x_0)}{\gamma^+(x)\gamma^-(x)}\ . \tag{2.13}$$

Because of (2.9), the Kramers-Moyal moments are related by[11]

$$A_1(x)=-\tfrac{1}{2}\bar{p}(x)^{-1}\sum_{n=1}^{\infty}\frac{1}{n!}\frac{1}{\Omega^n}\left[-\frac{\partial}{\partial x}\right]^n A_{n+1}(x)\bar{p}(x)\ . \tag{2.14}$$

On inserting (2.11) into (2.14) and passing to the limit $\Omega\to\infty$ we find

$$A_1(x)=-L(x)\chi_0(x)\ , \tag{2.15}$$

where we have introduced the generalized thermodynamic force

$$\chi_0(x)=\frac{\partial\phi_0(x)}{\partial x}=\ln\gamma^-(x)-\ln\gamma^+(x) \tag{2.16}$$

and where[8,11]

$$\begin{aligned}L(x)&=\tfrac{1}{2}\sum_{n=0}^{\infty}\frac{1}{(n+1)!}A_{n+2}(x)[\chi_0(x)]^n\\&=\frac{\gamma^+(x)-\gamma^-(x)}{\ln\gamma^+(x)-\ln\gamma^-(x)}\end{aligned} \tag{2.17}$$

is a transport coefficient. The second line shows that $L(x)>0$ since $(a-b)/(\ln a-\ln b)>0$ for all $a,b>0$. With (2.14) the deterministic law (2.8) takes the form of an Onsager-type transport law

$$\dot{x}=-L(x)\chi_0(x)\ . \tag{2.18}$$

This will be the starting point for the Fokker-Planck modeling put forward in Sec. III.

In general, the spectral properties of one-step Markov processes cannot be obtained exactly in the case of multistability. However, because of the strict detailed balancing, (2.9), the master operator in (2.1) can be symmetrized and its spectrum can be evaluated asymptotically for large Ω by means of the WKB method. For a bistable system the deterministic flow has a form as sketched in Fig. 1. There are two stable steady states at x_1 and x_2 and an unstable steady state at x_3. Following Matsuo[12] one finds for the spectrum in the limit $\Omega\to\infty$

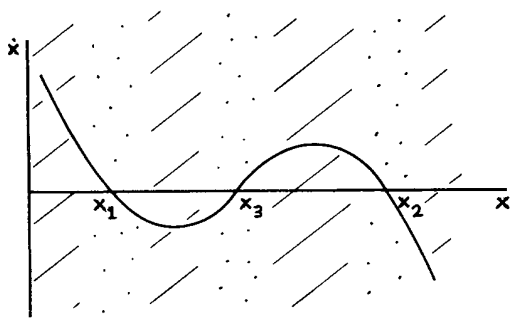

FIG. 1. Deterministic flow of a bistable system with drift-dominated regions (hatched) and diffusion-dominated regions (dotted).

$$\lambda_{1,n}=-n\lambda_1,\quad n=0,1,2,\ldots$$
$$\lambda_{2,n}=-n\lambda_2,\quad n=0,1,2,\ldots \tag{2.19}$$
$$\lambda_{3,n}=-(n+1)\lambda_3,\quad n=0,1,2,\ldots$$

where

$$\lambda_i=\left|\frac{\partial\dot{x}}{\partial x}\right|_{x=x_i},\quad i=1,2,3\ . \tag{2.20}$$

This result can also be derived by expanding the master equation in terms of Ω^{-1}. Putting

$$x(t)=x_i+\Omega^{1/2}y(t),\quad i=1,2,3 \tag{2.21}$$

one obtains in the limit $\Omega\to\infty$ a stable Ornstein-Uhlenbeck process $y(t)$ for $i=1,2$ and an unstable Ornstein-Uhlenbeck process for $i=3$ described by

$$\frac{\partial}{\partial t}\Pi_t(y)=\pm\lambda_i\frac{\partial}{\partial y}y\Pi_t(y)+\tfrac{1}{2}d_i\frac{\partial^2}{\partial y^2}\Pi_t(y)\ , \tag{2.22}$$

where

$$d_i=A_2(x_i)\ . \tag{2.23}$$

Here and in the following the upper sign holds for $i=1,2$ and the lower sign for $i=3$.

To find the right eigenfunctions we make the ansatz

$$\Pi_t(y)=e^{\lambda t}e^{\mp\lambda_i y^2/2d_i}\psi(y) \tag{2.24}$$

leading to the Schrödinger eigenvalue problem

$$\left[\tfrac{1}{2}d_i\frac{\partial^2}{\partial y^2}-\frac{\lambda_i^2}{2d_i}y^2\pm\frac{\lambda_i}{2}\right]\psi(y)=\lambda\psi(y)\ . \tag{2.25}$$

This gives the eigenvalues (2.19) and the eigenfunctions

$$\psi_{i,n}(y)=\frac{1}{2^n n!}e^{-\lambda_i y^2/2d_i}H_n\left[\left[\frac{\lambda_i}{d_i}\right]^{1/2}y\right], \tag{2.26}$$

where the H_n are Hermite polynomials.

This way the asymptotic right eigenfunctions $p_{i,n}(x)$ and left eigenfunctions $w_{i,n}(x)$ of the master operator in (2.4) are found to be

$$p_{i,n}(x)=\frac{1}{2^n n!}\left[\frac{\Omega\lambda_i}{\pi d_i}\right]^{1/2}e^{-(\Omega\lambda_i/d_i)(x-x_i)^2}\times H_n\left[\left[\frac{\Omega\lambda_i}{d_i}\right]^{1/2}(x-x_i)\right],\quad i=1,2$$
$$p_{3,n}(x)=\frac{1}{2^n n!}\left[\frac{\Omega\lambda_3}{\pi d_3}\right]^{1/2}H_n\left[\left[\frac{\Omega\lambda_3}{d_3}\right]^{1/2}(x-x_3)\right], \tag{2.27}$$

and

$$w_{i,n}(x)=H_n\left[\left[\frac{\Omega\lambda_i}{d_i}\right]^{1/2}(x-x_i)\right],\quad i=1,2$$
$$w_{3,n}(x)=e^{-(\Omega\lambda_3/d_3)(x-x_3)^2}H_n\left[\left[\frac{\Omega\lambda_3}{d_3}\right]^{1/2}(x-x_3)\right]. \tag{2.28}$$

For $\Omega\to\infty$ these eigenfunctions form a biorthonormal system

$$\int dx\, w_{i,n}(x)p_{j,m}(x)=\delta_{ij}\delta_{nm}\ ,$$
$$i,j=1,2,3,\quad n,m=0,1,2,\ldots\ . \tag{2.29}$$

While the asymptotic spectral properties of the master operator describe the behavior in the vicinity of the deterministic steady states x_i satisfactorily, global properties require a study of the (exponentially small) coupling between the three parts, $i=1,2,3$, of the asymptotic spectrum (2.19). Here, we shall restrict ourselves to a discussion of the effect of this coupling upon the degenerate eigenvalues $\lambda_{1,0}=\lambda_{2,0}=0$. The degeneracy is lifted by a tunnel-splitting. One eigenvalue will remain zero corresponding to the stationary probability $\bar{p}(x)$ and the other one will assume a small negative value λ_T. This eigenvalue can be expressed in terms of the transition rates $r(x_1\to x_2)=r^+$ and $r(x_2\to x_1)=r^-$ as

$$\lambda_T=-(r^++r^-)\ . \tag{2.30}$$

The rates $r^\pm$ themselves are related to mean first passage times. We will consider this relationship for r^+ only, since analogous arguments apply for r^-.

The site $N_3=\Omega x_3$ corresponds to the deterministically unstable steady state. For a process starting at a site N left of N_3 ($N<N_3$) we introduce the time $T(N)$ which the process needs on the average to reach for the first time the site N_3. For large Ω and for all starting points N (except those near N_3) the process will first follow the deterministic trajectory with a probability very close to 1. Then it will stay near the stable point $N_1=\Omega x_1$ for a very long time (much longer than the time in which N_1 was approached) before an occasional fluctuation drives the system to N_3. From there the system goes with equal probability to N_1 or N_2. The time needed for this last step is negligibly short compared with the sojourn time at N_1. Hence, the mean first passage time $T(N)$ is independent of N for most N and its constant part T determines the rate

$$r^+=\tfrac{1}{2}T^{-1}\ . \tag{2.31}$$

For one-step processes $T(N)$ has been evaluated in closed form[13,14]:

$$T(N)=\sum_{M=N}^{N_3-1}[W^+(M)\bar{P}(M)]^{-1}\sum_{K=0}^{M}\bar{P}(K)\ . \tag{2.32}$$

On the intensive scale we find in leading order for large Ω

$$T(x)=\Omega\int_x^{x_3}dy[\gamma^+(y)\bar{p}(y)]^{-1}\int_0^y dz\,\bar{p}(z)\ . \tag{2.33}$$

In view of (2.11), $T(x)$ becomes independent of x for $x_3-x>O(\Omega^{1/2})$, and its constant part T can further be simplified with the use of the method of steepest descent to yield

$$r^+=\frac{1}{2T}=\frac{1}{2\pi}\gamma^+(x_1)[\phi_0''(x_1)\,|\,\phi_0''(x_3)\,|\,]^{1/2}\times e^{-\Omega[\phi_0(x_3)-\phi_0(x_1)]}\ , \tag{2.34}$$

where ϕ_0'' denotes the second-order derivative, and where (2.11) and (2.13) and $\gamma^+(x_1)=\gamma^-(x_1)$ and $\gamma^+(x_3)=\gamma^-(x_3)$ have been used. Analogously, the rate r^- is found to be

$$r^- = \frac{1}{2\pi}\gamma^+(x_2)[\phi_0''(x_2) \mid \phi_0''(x_3) \mid]^{1/2} \times e^{-\Omega[\phi_0(x_3)-\phi_0(x_2)]} . \tag{2.35}$$

The small eigenvalue λ_T, (2.30), dominates the long-time behavior of bistable systems. Since this eigenvalue is well separated from the rest of the spectrum it is often related to macroscopically observable phenomena, e.g., the switching of tunnel diodes.

III. FOKKER-PLANCK MODELING

For large Ω one expects that the discrete nature of a Markov one-step process becomes unimportant and that the process can be approximated quite accurately by a continuous Markov process described by a Fokker-Planck equation. Since for nonlinear systems the Fokker-Planck equation is generally much more tractable than the master equation, the Fokker-Planck description enjoys great popularity. Hence, the question arises whether the Fokker-Planck equation gives results approaching those obtained from the master equation for large Ω.

Frequently, the Fokker-Planck modeling of nonlinear systems is based on the truncated Kramers-Moyal expansion (2.4) of the master equation. Retaining only the first two terms one finds

$$\frac{\partial}{\partial t}p_t(x) = -\frac{\partial}{\partial x}A_1(x)p_t(x) + \frac{1}{2\Omega}\frac{\partial^2}{\partial x^2}A_2(x)p_t(x) . \tag{3.1}$$

Since (2.6) gives

$$A_1(x)=\gamma^+(x)-\gamma^-(x), \quad A_2(x)=\gamma^+(x)+\gamma^-(x) , \tag{3.2}$$

the stationary probability of the Fokker-Planck equation (3.1) is found to be

$$\bar{p}(x)=[ZA_2(x)]^{-1}\exp[-\Omega\Psi_0(x)] , \tag{3.3}$$

where

$$\Psi_0(x) = -\int_{x_0}^{x} dy\, 2\frac{\gamma^+(y)-\gamma^-(y)}{\gamma^+(y)+\gamma^-(y)} . \tag{3.4}$$

Note that the potential $\Psi_0(x)$ differs from the correct potential $\phi_0(x)$, (2.12). This difference does not vanish in the limit $\Omega\to\infty$.

On the other hand, using a well-known expansion of the logarithm, we find

$$\chi_0(x) = \frac{\partial\phi_0(x)}{\partial x} = \frac{\partial\Psi_0(x)}{\partial x} - 2\sum_{l=1}^{\infty}\frac{1}{2l+1}\left[\frac{\gamma^+(x)-\gamma^-(x)}{\gamma^+(x)+\gamma^-(x)}\right]^{2l+1} . \tag{3.5}$$

Hence, at the steady states x_i of the deterministic motion both potentials are at extremes and their curvatures coincide:

$$\phi_0''(x_i)=\Psi_0''(x_i), \quad i=1,2,3 . \tag{3.6}$$

Furthermore, applying the method of Sec. II, it is easily seen that for $\Omega\to\infty$ the spectrum (2.19) and the eigenfunctions (2.27) and (2.28) are recovered from the Fokker-Planck equation (3.1).

The splitting of the degenerate eigenvalues $\lambda_{1,0}$ and $\lambda_{2,0}$ can again be calculated via mean first passage times. From (3.1) the time $T(x)$ which a process starting from $x<x_3$ needs to reach for the first time the instability point x_3 is obtained as[15]

$$T(x)=\Omega\int_x^{x_3} dy[\tfrac{1}{2}p(y)A_2(y)]^{-1}\int_0^y dz\,\bar{p}(z) . \tag{3.7}$$

Using (3.3) and $A_2(x_3)=2\gamma^+(x_3)=2\gamma^-(x_3)$, we obtain from (3.7) for large Ω the rate

$$r_{KM}^+ = \frac{1}{2\pi}\gamma^+(x_1)[\Psi_0''(x_1) \mid \Psi_0''(x_3) \mid]^{1/2} \times e^{-\Omega[\Psi_0(x_3)-\Psi_0(x_1)]} \tag{3.8}$$

and, correspondingly,

$$r_{KM}^- = \frac{1}{2\pi}\gamma^+(x_2)[\Psi_0''(x_2) \mid \Psi_0''(x_3) \mid]^{1/2} \times e^{-\Omega[\Psi_0(x_3)-\Psi_0(x_2)]} . \tag{3.9}$$

Comparison with (2.34) and (2.35) reveals that this result differs from the correct rates $r^\pm$ by a factor

$$r_{KM}^\pm = r^\pm e^{\Omega\Delta^\pm} , \tag{3.10}$$

where

$$\Delta^\pm = -2\sum_{l=1}^{\infty}\frac{1}{2l+1}\int_{x_{1,2}}^{x_3} dy\left[\frac{\gamma^+(y)-\gamma^-(y)}{\gamma^+(y)+\gamma^-(y)}\right]^{2l+1} > 0 . \tag{3.11}$$

In deriving this result we have taken advantage of (3.5) and (3.6). Thus, the Kramers-Moyal Fokker-Planck modeling overestimates the rates in leading order.

The shortcomings of the Kramers-Moyal Fokker-Planck modeling are due to the fact that the correct potential $\phi_0(x)$, (2.12), is not recovered. An alternative Fokker-Planck modeling, essentially overcoming this difficulty, has recently been put forward by Grabert, Hanggi, and Oppenheim.[8] Nonlinear transport theory[7] gives the connection between a deterministic description in terms of Onsager-type transport laws and a stochastic description in terms of a Fokker-Planck process. Based on this theory, the transport law (2.18) can be associated with the Fokker-Planck equation

$$\frac{\partial}{\partial t}p_t(x) = \frac{\partial}{\partial x}L(x)\left[\chi_0(x)+\frac{1}{\Omega}\chi_1(x)+\frac{1}{\Omega}\frac{\partial}{\partial x}\right]p_t(x) , \tag{3.12}$$

where

$$\chi_0(x)=\frac{\partial\phi_0(x)}{\partial x},\quad \chi_1(x)=\frac{\partial\phi_1(x)}{\partial x}\ . \tag{3.13}$$

Clearly, the stationary probability reads

$$\bar{p}(x)=Z^{-1}\exp\left[-\Omega\left[\phi_0(x)+\frac{1}{\Omega}\phi_1(x)\right]\right] \tag{3.14}$$

which coincides with the asymptotic stationary probability, (2.11), of the master equation. Furthermore, in the limit $\Omega\to\infty$ the stochastic process (3.12) reduces to a deterministic process described by (2.18). Because of (2.15) and (2.17), the new Fokker-Planck equation (3.12) may also be written

$$\frac{\partial}{\partial t}p_t(x)=-\frac{\partial}{\partial x}K_1(x)p_t(x)+\frac{1}{2\Omega}\frac{\partial^2}{\partial x^2}K_2(x)p_t(x)\ , \tag{3.15}$$

where

$$\begin{aligned}K_1(x)&=-L(x)\left[\chi_0(x)+\frac{1}{\Omega}\chi_1(x)\right]+\frac{1}{\Omega}\frac{\partial L(x)}{\partial x}\\&=A_1(x)+\frac{1}{\Omega}\left[\frac{\partial L(x)}{\partial x}-L(x)\chi_1(x)\right]\end{aligned} \tag{3.16}$$

and

$$\begin{aligned}K_2(x)&=2L(x)\\&=A_2(x)+\sum_{n=1}^{\infty}\frac{1}{(n+1)!}A_{n+2}(x)[\chi_0(x)]^n\ .\end{aligned} \tag{3.17}$$

This makes the difference with (3.1) more apparent. Note that the difference of the diffusion coefficients is not of order $1/\Omega$, but proportional to the deviation from steady states as measured by the thermodynamic force χ_0.

Before proceeding we note that, for any Fokker-Planck equation of the form (3.15) having the correct asymptotic stationary probability (2.11), the drift and diffusion coefficients are related by

$$K_1(x)=-\tfrac{1}{2}K_2(x)\frac{\partial\phi_0(x)}{\partial x}+O(1/\Omega)\ . \tag{3.18}$$

Since the deterministic law is recovered only if

$$K_1(x)=-L(x)\chi_0(x)+O(1/\Omega) \tag{3.19}$$

there follows

$$K_2(x)=2L(x)+O(1/\Omega)\ . \tag{3.20}$$

Hence, apart from terms of higher order in $1/\Omega$, the diffusion coefficient (3.17) is fixed by the stationary probability and the deterministic law. In particular, the postulate of a constant diffusion coefficient[16] is not valid, in general.

By means of the expansion (2.21) one readily shows that for $\Omega\to\infty$ the spectrum of the new Fokker-Planck equation (3.12) is again given by (2.19) with the asymptotic eigenfunctions (2.27) and (2.28). Furthermore, the mean first passage time $T(x)$ from an initial state $x<x_3$ to the instability point x_3 now reads

$$T(x)=\Omega\int_x^{x_3}dy[\bar{p}(y)L(y)]^{-1}\int_0^y dz\,\bar{p}(z) \tag{3.21}$$

which by virtue of (3.14) yields for large Ω the rate

$$\begin{aligned}r^+=&\frac{L(x_3)}{2\pi}[\phi_0''(x_1)\,|\,\phi_0''(x_3)\,|\,]^{1/2}\\&\times e^{-[\phi_1(x_3)-\phi_1(x_1)]}e^{-\Omega[\phi_0(x_3)-\phi_0(x_1)]}\ .\end{aligned} \tag{3.22}$$

With the use of (2.13) this may be written

$$\begin{aligned}r^+=&\frac{L(x_3)}{2\pi}\frac{\gamma^+(x_1)}{\gamma^+(x_3)}[\phi_0''(x_1)\,|\,\phi_0''(x_3)\,|\,]^{1/2}\\&\times e^{-\Omega[\phi_0(x_3)-\phi_0(x_1)]}\ ,\end{aligned} \tag{3.23}$$

where $\gamma^+(x_i)=\gamma^-(x_i)$ has been used. Since the latter relation gives

$$K_2(x_i)=2L(x_i)=A_2(x_i)=2\gamma^+(x_i)=2\gamma^-(x_i) \tag{3.24}$$

we see that (3.23) is identical with (2.34). The rate r^- can be determined correspondingly. Thus, the new Fokker-Planck equation yields the correct splitting of the lowest eigenvalue.

The diffusion coefficient of the Fokker-Planck equation (3.12) coincides with the second Kramers-Moyal moment in the vicinity of the steady states only. However, since the system rapidly leaves the drift-dominated regions (Fig. 1) between the steady states, the diffusion has a considerable effect on the dynamics in the diffusion-dominated regions only where it coincides with the diffusion obtained by means of Van Kampen's linearization scheme.[4] Consequently, the long-time behavior of the system can be recovered from the new Fokker-Planck modeling introduced in (3.12).

IV. SCHLÖGL MODELS

Schlögl[9] has introduced two models of chemical reactions describing a first- and second-order nonequilibrium phase transition, respectively. The Fokker-Planck description of these models will be studied by means of the approach put forward in Sec. III.

The first Schlögl model exhibits bistability and is characterized by the autocatalytic trimolecular reaction scheme

$$A+2X\underset{k_2}{\overset{k_1}{\rightleftarrows}}3X\ , \tag{4.1a}$$

$$A\underset{k_4}{\overset{k_3}{\rightleftarrows}}X\ . \tag{4.1b}$$

Let x and a denote the concentrations of the species X and A, respectively. The concentration a is held fixed, while x is the stochastic variable. Choosing the unit of time and the concentration a such that[9]

$$k_1A\Omega=3,\quad k_2\Omega^2=1\ , \tag{4.2}$$

where Ω is the volume, the master equation for the proba-

bility $P_t(N)$ to find N molecules of species X takes the form (2.1) with the transition probabilities

$$W^+(N)=k_3A+3N(N-1)/\Omega$$
$$=\Omega[\gamma^+(x)+\gamma_1^+(x)/\Omega], \quad (4.3a)$$
$$W^-(N)=k_4N+N(N-1)(N-2)/\Omega^2$$
$$=\Omega[\gamma^-(x)+\gamma_1^-(x)/\Omega+O(1/\Omega^2)], \quad (4.3b)$$

where

$$\gamma^+(x)=k_3a+3x^2, \quad (4.4a)$$
$$\gamma^-(x)=k_4x+x^3, \quad (4.4b)$$

and

$$\gamma_1^+(x)=-3x, \quad (4.5a)$$
$$\gamma_1^-(x)=-3x^2. \quad (4.5b)$$

The deterministic rate law (2.8) takes the form

$$\dot{x}=3x^2-x^3-k_4x+k_3a. \quad (4.6)$$

Depending on the parameters, there exist one or three steady states. Bistability with three steady states $x_1<x_3<x_2$ (Fig. 1) occurs for $k_4<3$ and sufficiently small k_3a.

From (4.4), we find for the potential (2.12)

$$\phi_0(x)=x(\ln x-1)+x\ln[(x^2+k_4)/(3x^2+k_3a)]$$
$$+2k_4^{1/2}\arctan(xk_4^{-1/2})$$
$$-2(k_3a/3)^{1/2}\arctan[x(k_3a/3)^{-1/2}]. \quad (4.7)$$

The correction term of order $1/\Omega$ follows from (2.13), (4.4), (4.5), and the expression given in Ref. 10 as

$$\phi_1(x)=\ln[(x^2+k_3a/3)/(x^2+k_4)]+\tfrac{1}{2}\ln(x/a), \quad (4.8)$$

where an irrelevant additive constant has been omitted. The stationary probability (3.14) is now found to read

$$\bar{p}(x)=\frac{x^2+k_4}{Zx^{1/2}(x^2+k_3a/3)}\exp[-\Omega\phi_0(x)]. \quad (4.9)$$

Introducing the thermodynamic force (2.16)

$$\chi_0(x)=\ln[x(x^2+k_4)/(3x^2+k_3a)] \quad (4.10)$$

and the transport coefficient (2.17)

$$L(x)=\frac{x^3-3x^2+k_4x-k_3a}{\ln[(x^3+k_4x)/(3x^2+k_3a)]}, \quad (4.11)$$

the deterministic law (4.6) may be written in the form (2.18) of a transport equation. Finally, with the use of (3.13) and (4.8), the $1/\Omega$ correction to the thermodynamic force is readily evaluated, which in connection with (4.10) and (4.11) determines the Fokker-Planck equation (3.12).

In the bistable region, the rate r^+ for transitions from x_1 to x_2 can now be determined from (3.22). After some algebra one obtains

$$r^+=\frac{[(\gamma_1^2-\alpha x_1^3)\,|\,\gamma_3^2-\alpha x_3^3\,|\,]^{1/2}}{2\pi x_3^2(x_1^2+k_4)}e^{-\Omega[\phi_0(x_3)-\phi_0(x_1)]}, \quad (4.12)$$

where $\gamma_i=\gamma^+(x_i)=\gamma^-(x_i)$ and $\alpha=6k_4-2k_3a$. For large Ω, (4.12) coincides precisely with the activation rate of the master equation as determined from (2.33) and (4.9). The result in (4.12) remains true for the activation rate r^-: The equation is only subjected to the trivial replacement $x_1\to x_2$. The same method can be applied to a variety of other discontinuous transitions, e.g., optical bistabilities[17] and bistable tunnel diodes.[18]

In his second model, Schlögl has introduced a simple autocatalytic reaction scheme describing a continuous nonequilibrium phase transition[9]

$$X+A\underset{k^-}{\overset{k^+}{\rightleftarrows}}2X, \quad (4.13a)$$
$$X+B\overset{k'}{\to}C. \quad (4.13b)$$

Let x, a, and b denote the concentrations of the species X, A, and B, respectively. Choosing the unit of time and the concentration a such that

$$k^-=1,\quad k^+a=1, \quad (4.14)$$

the master equation for the probability $P_t(N)$ to find N molecules of species X takes the form (2.1) with

$$W^+(N)=N, \quad (4.15a)$$
$$W^-(N)=\eta N+\frac{N(N-1)}{\Omega}, \quad (4.15b)$$

where

$$\eta=k'b. \quad (4.16)$$

Since $W^+(0)=0$, the state $N=0$ is an absorbing state, and the stationary probability reads

$$\bar{P}(N)=\delta_{N,0}. \quad (4.17)$$

The Schlögl model has an absorbing state only because the backward reaction of (4.13b) is disregarded. However, the same problem may occur without making approximations, as, for instance, in most problems of population dynamics.[19]

The transition probabilities (4.15) satisfy the scaling (2.2) with[10]

$$\gamma^+(x)=x,\quad \gamma^-(x)=\eta x+x^2,\quad \gamma_1^-(x)=-x. \quad (4.18)$$

Hence, the deterministic law (2.8) reads

$$\dot{x}=(1-\eta)x-x^2. \quad (4.19)$$

For $\eta\geq 1$ there is one steady state $x_1=0$ which is stable, while for $0<\eta<1$ there are two steady states $x_1=0$ and $x_2=1-\eta$, the first being unstable and the latter being stable. Since (4.17) is the unique stationary distribution of the master equation, the stochastic theory has only one steady state, $x_1=0$, for all $\eta>0$, and there seems to be a contradiction with the above findings for $0<\eta<1$.

Restricting the state space to $1 \leq N < \infty$ by making $N=1$ a reflecting state,[20] the process possesses a normalizable stationary probability of the form (2.11). By use of (4.18) we find for the potential (2.12)

$$\phi_0(x)=(x+\eta)\ln(x+\eta)-x \tag{4.20}$$

and for the potential (2.13), utilizing Ref. 10

$$\phi_1(x)=\ln x-\tfrac{1}{2}\ln(x+\eta)\ , \tag{4.21}$$

yielding for the stationary probability $\bar{p}(x)$ defined on the interval $1/\Omega \leq x < \infty$

$$\bar{p}(x)=(Zx)^{-1}(x+\eta)^{1/2}\exp[-\Omega\phi_0(x)]\ . \tag{4.22}$$

Now, in terms of the thermodynamic force (2.16)

$$\chi_0(x)=\frac{\partial\phi_0}{\partial x}=\ln(x+\eta) \tag{4.23}$$

and the transport coefficient (2.17)

$$L(x)=x(\eta+x-1)/\ln(x+\eta)\geq 0 \tag{4.24}$$

the deterministic flow (4.19) may be written in the form of a transport law

$$\dot{x}=-L(x)\chi_0(x)\ . \tag{4.25}$$

Following the reasoning in Sec. III, we again introduce a Fokker-Planck equation of the form (3.12) which for the present problem reads

$$\frac{\partial}{\partial t}p_t(x)=\frac{\partial}{\partial x}\frac{x(x+\eta-1)}{\ln(x+\eta)} \times\left[\ln(x+\eta)+\frac{1}{\Omega}\frac{x+2\eta}{2x(x+\eta)}+\frac{1}{\Omega}\frac{\partial}{\partial x}\right]p_t(x)\ . \tag{4.26}$$

The probability distribution (4.22) is the unique stationary distribution of (4.26) normalizable in the interval $1/\Omega \leq x < \infty$. This distribution is not normalizable in the full interval $0 \leq x < \infty$, however, indicating the existence of the absorbing state $x=0$. The truncated Kramers-Moyal expansion also leads to a stationary distribution which is not normalizable in the full interval,[21] but with a different potential in the exponent.

For a process starting at the state N, the mean absorption time $T(N)$ which elapses on the average before the system is absorbed at $N=0$ is given by [cf. (2.32)]

$$T(N)=\sum_{M=1}^{N}[W^{-}(M)\tilde{P}(M)]^{-1}\sum_{K=M}^{\infty}\tilde{P}(K)\ , \tag{4.27}$$

where $\tilde{P}(N)$ is defined by (2.10), i.e.,

$$\tilde{P}(N)=\tilde{P}(1)\prod_{M=1}^{N-1}\frac{M}{\eta(M+1)+M(M+1)/\Omega}\ . \tag{4.28}$$

Note that the master equation has the unique stationary solution (4.17), while $\tilde{P}(N)$ is a quasistationary solution, the logarithm of which coincides with $\ln\bar{p}(x)$ in (4.22) up to order $1/\Omega$. On the intensive scale, we obtain for the mean absorption time for large Ω in leading order

$$T(x)=\Omega\int_0^x dy\,[y(y+\eta)\bar{p}(y)]^{-1}\int_y^{\infty}dz\,\bar{p}(z)\ . \tag{4.29}$$

This expression is well defined because $y(y+\eta)\bar{p}(y)$ is finite at $y=0$. From the Fokker-Planck equation (4.26) we obtain for the mean absorption time without further approximation

$$T_{\mathrm{FP}}(x)=\Omega\int_0^x dy\frac{\ln(y+\eta)}{y(1+\eta-y)\bar{p}(y)}\int_y^{\infty}dz\,\bar{p}(z)\ . \tag{4.30}$$

For $0<\eta<1$, the two expressions $T(x)$ and $T_{\mathrm{FP}}(x)$ are exponentially large in Ω with the same Arrhenius factor $\exp(\Omega\Delta\phi_0)$ where

$$\Delta\phi_0=\eta\ln\eta+1-\eta>0\ . \tag{4.31}$$

The prefactors do not coincide, however, because around $x=1/\Omega$ a relation corresponding to (3.24) does not hold.

In summary, we conclude that the newly proposed Fokker-Planck modeling yields asymptotically correct escape times for bistable systems and even gives the correct leading order term of the absorption time in systems dying out, although the latter are not precisely in the range of application of our method.

V. GENERALIZATIONS AND LIMITATIONS

In the foregoing sections, we have discussed one-dimensional one-step processes only. In this case, the process automatically satisfies strict detailed balance, i.e., the transformation

$$[\bar{P}(\vec{\mathrm{M}})]^{-1/2}W(\vec{\mathrm{M}}\rightarrow\vec{\mathrm{N}})[\bar{P}(\vec{\mathrm{N}})]^{1/2}$$

explicitly symmetrizes the master operator implying real eigenvalues.[3] In the presence of strict detailed balance, a Fokker-Planck modeling of multidimensional Markov processes, eventually with multistep transitions, can be obtained by a straightforward extension of the method presented in Sec. III. On the intensive scale $\vec{x}=\vec{\mathrm{N}}/\Omega$ the stationary probability of the master equation may be written

$$\bar{p}(\vec{x})=Z^{-1}\exp\left\{-\Omega\left[\phi_0(\vec{x})+\frac{1}{\Omega}\phi_1(\vec{x})+O\left[\frac{1}{\Omega^2}\right]\right]\right\}\ . \tag{5.1}$$

The thermodynamic forces $\chi_i^0(\vec{x})$ are again defined as derivatives of the potential $\phi_0(\vec{x})$ by

$$\chi_i^0(\vec{x})=\frac{\partial}{\partial x_i}\phi_0(\vec{x})\ . \tag{5.2}$$

Further, in terms of the Kramers-Moyal moments $A_{i_1\cdots i_n}(\vec{x})$, an Onsager-type transport matrix can be defined by[11]

$$L_{ij}(\vec{x})=\tfrac{1}{2}\left[A_{ij}^0(\vec{x})+\sum_{n=1}^{\infty}\frac{1}{(n+1)!}A_{iji_1\cdots i_n}^0(\vec{x})\times\chi_{i_1}^0(\vec{x})\cdots\chi_{i_n}^0(\vec{x})\right]\ , \tag{5.3}$$

where $A^0_{i_1\cdots i_n}(\vec{x})$ denotes the limit for $\Omega\to\infty$ of the Kramers-Moyal moments. The limiting deterministic law for $\Omega\to\infty$ may then be written

$$\dot{x}_i=-\sum_j L_{ij}(\vec{x})\chi^0_j(\vec{x})\ . \tag{5.4}$$

Again, the transport matrix determines the diffusion matrix of the Fokker-Planck equation,[8] which now takes the form

$$\frac{\partial}{\partial t}p_t(\vec{x})=\sum_{i,j}\frac{\partial}{\partial x_i}L_{ij}(\vec{x})\left[\chi^0_j(\vec{x})+\frac{1}{\Omega}\chi^1_j(\vec{x})+\frac{1}{\Omega}\frac{\partial}{\partial x_j}\right]p_t(\vec{x})\ . \tag{5.5}$$

This equation has (5.1) as a stationary solution and reduces to the deterministic law (5.4) for $\Omega\to\infty$.

The situation is more complicated if detailed balance does not hold in the strict sense. We have been able to extend our method to particular models without detailed balance but a general scheme has not been found. We hope to return to this problem in a future publication.

ACKNOWLEDGMENTS

This work has been supported by the Swiss National Science Foundation and the Deutsche Forschungsgemeinschaft.

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$$W^{\pm}(N)=\Omega[\gamma^{\pm}(x)+(1/\Omega)\gamma^{\pm}_1(x)+O(1/\Omega^2)]$$

the additional term

$$\int_{x_0}^{x}dy[\gamma^-_1(y)\gamma^+(y)-\gamma^+_1(y)\gamma^-(y)]/\gamma^+(y)\gamma^-(y)$$

appears in $\phi_1(x)$.
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