ARTICLES

Stationary probability distribution near stable limit cycles far from Hopf bifurcation points

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We obtain analytic results for the stationary probability distribution in the vicinity of a stable limit cycle for Markov systems described by a Fokker-Planck equation or a birth-death master equation. The results apply best for ranges of parameters removed from Hopf bifurcation points. As a by-product, we demonstrate that there holds a Liouville-like theorem for the stationary probability distribution: the product of the velocity along the limit cycle times the area of the cross section of the probability distribution transverse to the cycle is a constant. A numerical simulation of a chemical model system with a limit cycle shows good agreement with the analytic results.

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I. INTRODUCTION

The time evolution of the averages in physical and chemical oscillatory systems is described by deterministic equations which, for homogeneous (spatially uniform) systems, are usually ordinary differential equations. The stochastic approach considers fluctuations from the macroscopic averages (of concentrations, or other state variables), and a probability distribution is defined which satisfies stochastic equations of one or another form. Analytic solutions for time-dependent probability distributions, which describe the relaxation either to a stationary or a nonstationary attractor such as a limit cycle, are hardly available. For systems with detailed balance, in particular for some one-variable systems that possess single or multiple stationary states, an analytic solution is known for the time-independent stationary probability distribution.

In this paper, we present an approximate analytic solution for the stationary probability distribution density for a system with a stable limit cycle. We assume that this probability density satisfies a Fokker-Planck equation with state-dependent probability diffusion coefficients. The stochastic analysis of chemical systems is usually based on master equations describing birth-death processes; in the thermodynamic limit of fluctuations small compared to macroscopic averages (of the order of the square root of the reciprocal size of the system) such master equations can be transformed to Fokker-Planck equations. We obtain an approximate analytic solution in the vicinity of the limit cycle by using transformation of variables; illustrate the use of the general expressions with a specific example, a two-variable Selkov model with a limit cycle; and compare the results of the analytic solution to numerical calculations. The analytic solution agrees well with the numerical results.

Former analytic work on the probability distribution of the fluctuations in systems with limit cycles was focused primarily on the cases where the equations of motion were in normal form, so that the radial motion is separable from the angular motion and the angular velocity is independent of the angle. The first results have been obtained in the middle 1950s [1] in the context of fluctuations in radio frequency generators. A detailed analysis of the problem was done later on in the context of fluctuations in lasers (see [2–4] and references therein) and also in the context of limit cycles in chemical systems near bifurcation point (see [5–8] and references therein). The probability density distribution is of the shape of a circular or nearly circular crater, with the ridge of the crater corresponding to the deterministic trajectory of the limit cycle. The fact that a system is close to a Hopf bifurcation point makes it reasonable not only to use the normal form but also to assume that the "stiffness" of the system in the radial direction is small; hence the motion in this direction is slow compared to the motion along the limit cycle and the fluctuations are comparatively large. The corrections to the probability density distribution due to the angular velocity of the rotation being weakly dependent on the radius and on the angle were considered in Ref. [9] (see also Ref. [10] where a systematic approach is suggested to the analysis of the form of the probability distribution near Hopf bifurcation points).

For a fully developed limit cycle the motion towards and along the limit cycle are not separable, which makes analysis more complicated. There are some numerical simulations of the probability distribution of fluctuations (as described by a master equation or a Fokker-Planck equation) of systems with a limit cycle far from a Hopf bifurcation point [7,11,12]. All these numerical simula-

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tions confirmed that there exists a stable stationary probability distribution for such system, and this distribution is crater shaped, with the uneven ridge of the crater being the deterministic limit cycle.

The analysis of the present paper applied to limit cycles far from a bifurcation point; it is restricted to small fluctuations from the attractor-limit cycle, where the shape of the distribution in the directions transverse to the limit cycle is Gaussian. In Sec. II, we give the general formulation and approximate analytic solution for the stationary probability density distribution of a Markov system with a stable limit cycle. As a by-product of our theory, we prove a theorem which states that the product of the on-cycle velocity times the area of the cross section of the probability density is constant along the limit cycle. In Sec. III, the general theory is specified and applied to a simple two-variable chemical system. We compare our analytic results with numerical simulations and summarize our results in Sec. IV.

II. GENERAL CASE

A. Deterministic equations

Consider an autonomous dynamical system, in which x_i represents the concentration of a chemical species i ($i=1,\ldots,N$) or other state variable; the dynamic equations are of the form

$$\frac{dx_i}{dt}=A_i(x_1,\ldots,x_N) \quad (N\geq 2) \tag{2.1}$$

and we suppose that a solution exists which is a stable limit cycle. We choose now another set of variables $(\xi_1,\ldots,\xi_N)$ and the transformation between the set $(x_1,\ldots,x_N)$ and the set $(\xi_1,\ldots,\xi_N)$ is given by

$$B_{ij}=\frac{\partial x_i}{\partial \xi_j} \ . \tag{2.2}$$

We impose the requirement that the coordinates $(\xi_1,\ldots,\xi_N)$ are perpendicular to each other, which we can achieve with the orthogonal unitary transformation matrix

$$\sum_k B_{ik}B_{jk}=\delta_{ij} \ . \tag{2.3}$$

The dynamic equations, Eq. (2.1), in terms of the ξ variables are

$$\frac{d\xi_i}{dt}=\sum_j (B^{-1})_{ij}A_j=\sum_j B_{ji}A_j \ . \tag{2.4}$$

To describe the motion in the close vicinity of the limit cycle we choose the first coordinate ξ_1 as the length along the limit cycle in the phase space. When the system is on the attractor, the limit cycle, the speed of the system on the cycle is V,

$$\frac{d\xi_1}{dt}=V \ , \quad V\equiv V(\xi_1)=\left[\sum_i A_i^2\right]^{1/2} , \tag{2.5}$$

where the $A_i(\mathbf{x})$ are evaluated for the values $(x_1,\ldots,x_N)$ on the cycle and therefore depend on the ξ_1 only. It follows from Eqs. (2.4) and (2.5) that, on the limit cycle,

$$(B^{-1})_{1j}=\frac{A_j}{V} \ . \tag{2.6}$$

This equation establishes the first row of the matrix B^{-1}. Hence by using Schmitz's procedure, we can find the elements of the matrix B^{-1} in all other rows on the limit cycle, and thus establish the local transformation from the $\mathbf{x}$ coordinates to the ξ coordinates, with each ξ coordinate perpendicular to all other ξ coordinates. On the limit cycle ξ_1 varies in time but the remaining coordinates $(\xi_2,\ldots,\xi_N)$ are constant,

$$\frac{d\xi_i}{dt}=\sum_{j\,(\geq 1)} B_{ji}A_j=0 \quad (\text{on cycle, } i>2) \ . \tag{2.7}$$

We choose the origin of the coordinates $(\xi_2,\ldots,\xi_N)$ on the limit cycle, i.e., $\xi_2=\cdots=\xi_N=0$ along the cycle.

In a close vicinity of the limit cycle, we may carry out a Taylor expansion,

$$\sum_{j\,(\geq 1)} B_{ji}A_j=\sum_{\substack{k\,(\geq 2)\\ j\,(\geq 1)}} B_{ji}\xi_k\frac{\partial}{\partial \xi_k}A_j =\sum_{\substack{k\,(\geq 2)\\ j,l\,(\geq 1)}} B_{ji}B_{lk}\frac{\partial A_i}{\partial x_l}\xi_k \quad (i\geq 2) \ , \tag{2.8}$$

where the derivatives are evaluated on the limit cycle. The deterministic equation for the variables $(\xi_2,\ldots,\xi_N)$ for small $|\xi_2|,\ldots,|\xi_N|$ are

$$\frac{d\xi_i}{dt}=-\sum_{k\,(\geq 2)} L_{ik}\xi_k \quad (i\geq 2) \ , \tag{2.9}$$

where

$$L_{ik}=-\sum_{j,l} B_{ji}B_{lk}\frac{\partial A_j}{\partial x_l} \quad (i\geq 2, k\geq 2) \ . \tag{2.10}$$

The stability of the limit cycle requires that a deterministic trajectory gets closer to the limit cycle after a turn, i.e., $|\xi_j|$ decreases after a turn for $j\geq 2$. The consequence of this stability requirement will be discussed in the Appendix.

B. Stationary Fokker-Planck equation

For chemical limit cycles the probability distribution of chemical species is described by a birth-death master equation, and the time variation of the distribution is given by

$$\frac{d}{dt}P(\mathbf{X},t)=\sum_{\mathbf{X}'} W(\mathbf{X}|\mathbf{X}')P(\mathbf{X}',t)-\sum_{\mathbf{X}'} W(\mathbf{X}'|\mathbf{X})P(\mathbf{X},t) \ , \tag{2.11}$$

where $\mathbf{X}=(X_1,\ldots,X_N)$, $X_i=x_i\Omega$ is the number of molecules of the species i, x_i is the number density, and Ω the volume of the system. Kinetic equations, whether of the master equation or Fokker-Planck type (see below), have stable stationary solution for probability distributions, even though the deterministic system may have no stable stationary solution. Since we are interested in the stationary distribution only, we set the left-hand side of Eq. (2.11) to be equal to zero. In the thermodynamic limit this stationary difference equation can be approximated by a differential one, allowing for the smallness of fluctuations which are of the order of the inverse square root of the volume of the system, $1/\Omega^{1/2}$. The resulting equation, to Gaussian approximation, comes to a stationary Fokker-Planck equation,

$$-\sum_i \frac{\partial}{\partial x_i} A_i(\mathbf{X})P(\mathbf{x})+\sum_{i,j}\frac{\partial^2}{\partial x_i \partial x_j}D_{ij}(\mathbf{x})P(\mathbf{x})=0 , \quad (2.12)$$

where D_{ij} is the probability diffusion coefficient of the system and is of the order of $1/\Omega$. There are discussions [13] about the justification of the transformation from a time-dependent master equation to a time-dependent Fokker-Planck equation for systems with stable limit cycle. We consider only stationary distribution, and we shall see *a posteriori* that the stationary solution obtained satisfies not only the stationary Fokker-Planck equation Eq. (2.12), but also the stationary master equation.

Fokker-Planck equations are used to describe not only chemical reactions, but also transport processes, electronic circuits, lasers, Josephson junctions, etc. [14]. For a noise driven system, the Fokker-Planck equation for the probability density can be obtained from stochastic differential (Langevin) equations. In this case the probability diffusion coefficients D_{ij} are proportional to the intensity of the noise and may be state dependent or state independent, depending on the properties of the noise in the system. We assume that the parameter $\Omega^{-1}\sim|D_{ij}|$ is the small parameter of the system; on application to chemical kinetics we call Ω the volume of the system, although it might also be the reciprocal noise intensity.

In the thermodynamic limit $\Omega\to\infty$, the amplitudes of the fluctuations away from the attractor are small, and hence transforming into ξ coordinate, we may write the first term in Eq. (2.12) as

$$\sum_i \frac{\partial}{\partial x_i} A_i(\mathbf{x})P(\mathbf{x})=\sum_i \left[\frac{\partial}{\partial x_i}A_i(\mathbf{x})\right]P(\xi)+V\frac{\partial}{\partial \xi_1}P(\xi) - \sum_{i,k\ (\geq 2)} \xi_k L_{ik}\frac{\partial}{\partial \xi_i}P(\xi) . \quad (2.13)$$

The second term in Eq. (2.12) can be transformed in the similar way. Hence the stationary Fokker-Planck equation in the vicinity of the limit cycle reads

$$-\sum_i \left[\frac{\partial}{\partial x_i}A_i(\mathbf{x})\right]P(\xi)-V\frac{\partial}{\partial \xi_1}P(\xi)+\sum_{i,k\ (\geq 2)}\xi_k L_{ik}\frac{\partial}{\partial \xi_i}P(\xi)+\sum_{i,j,k,l}(B^{-1})_{ki}(B^{-1})_{lj}\left[\frac{\partial^2}{\partial \xi_k \partial \xi_l}D_{ij}(\xi)P(\xi)\right]=0 . \quad (2.14)$$

The stationary probability density distribution for a system with a limit cycle shows a volcano-shaped crater, with the ridge of the crater coinciding with the deterministic trajectory of the limit cycle [1,2,7,11–13]. The change of the probability density along the ridge of the crater is smooth, and that in the direction perpendicular to the cycle is very steep. Correspondingly, we seek a stationary solution of the form

$$P(\xi)=H(\xi_1)\exp\left[\Omega \sum_{i,j\ (\geq 2)}\gamma_{ij}(\xi_1)\xi_i\xi_j\right] , \quad (2.15)$$

where $\gamma_{ij}=\gamma_{ji}$ by construction. In Eq. (2.15) we postulate a Gaussian distribution in a section through the attractor perpendicular to the ξ_1 axis. The amplitude of the fluctuations away from the attractor depends on Ω and is of the order of the width of the crater, i.e., of the order of $1/\Omega^{1/2}$, and therefore we have

$$\frac{\partial}{\partial \xi_1}P(\xi)=P(\xi)\left[\frac{d\ln H}{d\xi_1}+\Omega\sum_{i,j}\xi_i\xi_j\frac{d\gamma_{ij}}{d\xi_1}\right]\sim P(\xi) , \quad (2.16)$$

$$\frac{\partial}{\partial \xi_i}P(\xi)=2\Omega\sum_{m\ (\geq 2)}\gamma_{mi}(\xi_1)P(\xi)\xi_m\sim\Omega^{1/2}P(\xi) \quad (i\geq 2) . \quad (2.17)$$

The only part in the diffusion term in Eq. (2.14) that survives in the limit $\Omega\to\infty$ (for $|\xi_2|,\ldots,|\xi_N|\sim\Omega^{-1/2}$) is

$$D_{ij}(\xi)\frac{\partial^2}{\partial \xi_k\partial \xi_l}P(\xi)\approx D_{ij}(\xi)P(\xi) \times\left\{4\Omega^2\sum_{m,n\ (\geq 2)}\gamma_{mk}\xi_m\gamma_{nl}\xi_n +2\Omega\gamma_{lk}\right\} . \quad (2.18)$$

Since $D_{ij}(\xi)$ is a smooth function of the variables and the actual $|\xi_{j\geq 2}|$ are very small, we can replace, within the approximation adopted, $D_{ij}(\xi_1,\xi_2,\ldots,\xi_N)$ by its value on the cycle $\bar{D}_{ij}(\xi_1)=D_{ij}(\xi_1,0,\ldots,0)$. Then the stationary Fokker-Planck equation takes the form

$$-\sum_i \left[\frac{\partial}{\partial x_i}A_i(\mathbf{x})\right]P(\xi)-VP(\xi)\left[\frac{d\ln H}{d\xi_1}+\sum_{i,j\,(\geq 2)}\Omega\xi_i\xi_j\frac{d\gamma_{ij}}{d\xi_1}\right]+2\Omega\sum_{\substack{i,k,m\,(\geq 2)\\ j,l}}\xi_k\xi_m\gamma_{mi}L_{ik}P(\xi)$$
$$+\sum_{\substack{k,l\,(\geq 2)\\ i,j}}(B^{-1})_{ki}(B^{-1})_{lj}\bar{D}_{ij}(\xi_1)P(\xi)\left[4\Omega^2\sum_{n,m\,(\geq 2)}\gamma_{nk}\xi_n\gamma_{ml}\xi_m+2\Omega\gamma_{lk}\right]=0\ . \quad (2.19)$$

Equation (2.19) can be separated into two groups of ordinary differential equations: those equations being quadratic in ξ_i ($i\geq 2$) with only $\gamma_{ij}(\xi_1)$ as unknown,

$$-V\frac{d\hat{\gamma}}{d\xi_1}+\hat{\gamma}\hat{L}+\hat{L}^\dagger\hat{\gamma}+2\hat{\gamma}\hat{M}\hat{\gamma}=0\ , \quad (2.20)$$

and the equation for the terms of zeroth power in ξ_i ($i\geq 2$) with both $\gamma_{ij}(\xi_1)$ and $H(\xi_1)$ as unknowns,

$$-\sum_i\left[\frac{\partial}{\partial x_i}A_i(\mathbf{x})\right]-V\frac{d\ln H}{d\xi_1}+\mathrm{Tr}(\hat{M}\hat{\gamma})=0\ . \quad (2.21)$$

Here the hat is used for matrices. The matrix $\hat{L}$ has been defined in Eq. (2.10), whereas the matrix $\hat{M}$ is

$$M_{kl}=M_{kl}(\xi_1)=2\Omega\sum_{i,j}(B^{-1})_{ki}(B^{-1})_{lj}\bar{D}_{ij}(\xi_1)$$
$$(k\geq 2, l\geq 2)\ . \quad (2.22)$$

The matrix $\hat{M}$ is symmetrical and positive definite, whereas the matrix $\hat{L}$ is not, in general. Since both $\hat{M}$ and $\hat{L}$ are defined on the cycle they are both periodic,

$$\hat{L}(\xi_1)=\hat{L}(\xi_1+L)\ ,\quad \hat{M}(\xi_1)=\hat{M}(\xi_1+L)\ , \quad (2.23)$$

where L is the length of the limit cycle along the variable ξ_1.

By multiplying Eq. (2.20) on the left and right by $\hat{\gamma}^{-1}$ we arrive at a *linear* equation for the matrix $\hat{\gamma}^{-1}$:

$$V\frac{d\hat{\gamma}^{-1}}{d\xi_1}+\hat{L}\hat{\gamma}^{-1}+\hat{\gamma}^{-1}\hat{L}^\dagger+2\hat{M}=0\ . \quad (2.24)$$

The requirement of the distribution $P(\xi_1,\ldots,\xi_N)$ to be single valued gives the boundary conditions for Eqs. (2.20), (2.21), and (2.24),

$$\hat{\gamma}(\xi_1)=\hat{\gamma}(\xi_1+L)\ ,\quad \hat{H}(\xi_1)=\hat{H}(\xi_1+L)\ . \quad (2.25)$$

The existence of a solution satisfying the periodic boundary conditions, Eq. (2.25), for Eq. (2.24) is guaranteed by the fact that all the coefficient matrices in Eqs. (2.20) and (2.21) are periodic. In the Appendix, we prove that the matrix $-\hat{\gamma}$ is positive definite, which is a prerequisite for the solution of the form Eq. (2.15) to be meaningful.

From Eq. (2.21) we can express $H(\xi_1)$ in terms of $\gamma_{ij}(\xi_1)$,

$$\ln\frac{H(\xi_1)}{H(0)}=\int_0^{\xi_1}d\xi_1\frac{1}{V}\left[\mathrm{Tr}(\hat{M}\hat{\gamma})-\sum_i\left[\frac{\partial}{\partial x_i}A_i(\mathbf{x})\right]\right]\ ; \quad (2.26)$$

the constant $H(0)$ is determined by the normalization condition

$$\left[\frac{\pi}{\Omega}\right]^{(N-1)/2}\int_0^L d\xi_1|\det\hat{B}|\,|\det\hat{\gamma}|^{-1/2}H(\xi_1)=1\ . \quad (2.27)$$

Equations (2.15), (2.20), (2.26), and (2.27) give in explicit form the stationary probability distribution for small fluctuations from the attractor, for systems with stable limit cycle, far from a Hopf bifurcation point.

C. A Liouville-type theorem

From numerical solutions of the stationary probability distribution as given by a master equation or a Fokker-Planck equation for an oscillatory system, we have observed that

$$\sigma(\xi_1)V(\xi_1)\approx\text{const}\ , \quad (2.28)$$

where $\sigma(\xi_1)$ is the area of the cross section of the crater-shaped probability distribution at a given ξ_1.

$$\sigma(\xi_1)=\int_{-\infty}^{\infty}P(\xi_1,\xi_2,\ldots,\xi_N)d\xi_2\cdots d\xi_N\ , \quad (2.29)$$

and $V(\xi_1)$ is the velocity along the cycle, also at ξ_1. As a by-product of our approximate analytic solution, Eqs. (2.15), (2.20), and (2.26), we can prove a theorem, which confirms our estimate from numerical solutions. From the stationary Fokker-Planck equation, Eq. (2.14), with consideration of Eqs. (2.15) and (2.18), we have

$$-\sum_i\left[\frac{\partial}{\partial x_i}A_i(\mathbf{x})\right]P(\xi)-V\frac{\partial}{\partial\xi_1}P(\xi)$$
$$+\sum_{i,k\,(\geq 2)}\xi_kL_{ik}\frac{\partial}{\partial\xi_i}P(\xi)$$
$$+\frac{1}{2\Omega}\sum_{k,l\,(\geq 2)}M_{kl}\left[\frac{\partial^2}{\partial\xi_k\partial\xi_1}P(\xi)\right]=0\ . \quad (2.30)$$

We now integrate Eq. (2.30) with respect to $(\xi_2,\ldots,\xi_N)$ over the range $(-\infty,\infty)$ for each variable, allowing for the fact that $P(\xi_1,\xi_2,\ldots,\xi_N)\to 0$ for $|\xi_{i\geq 2}|\to\infty$. The last term in Eq. (2.30) vanishes and the third term becomes

$$\int\sum_{i,k\,(\geq 2)}\xi_kL_{ik}\frac{\partial}{\partial\xi_i}P(\xi)d\xi_2d\xi_3\cdots d\xi_N$$
$$=-\sigma(\xi_1)\sum_{k\,(\geq 2)}L_{kk}$$
$$=\sigma(\xi_1)\sum_i\frac{\partial A_i}{\partial x_i}-\sigma(\xi_1)\frac{\partial V}{\partial\xi_1}\ . \quad (2.31)$$

Hence after integration, Eq. (2.30) reads

$$0=-\sum_i\left[\frac{\partial}{\partial x_i}A_i(\mathbf{x})\right]\sigma(\xi_1)-V\frac{\partial}{\partial\xi_1}\sigma(\xi_1)+\sigma(\xi_1)\sum_i\frac{\partial A_i}{\partial x_i}-\sigma(\xi_1)\frac{\partial V}{\partial\xi_1}=-\frac{d}{d\xi_1}[\sigma(\xi_1)V] , \tag{2.32}$$

that is

$$\sigma(\xi_1)V(\xi_1)\equiv V(\xi_1)H(\xi_1)(\pi/\Omega)^{(N-1)/2}|\det\hat{\gamma}|^{-1/2}=\text{const} \tag{2.33}$$

on the limit cycle at every value of ξ_1. This result follows also from the explicit form of $H(\xi_1)$ (2.26) with account taken of (2.24),(2.31). It is similar to Liouville's theorem of conservation of phase volume of Hamiltonian systems in classical mechanics: in the present case, the probability flux through a cross section is conserved.

III. TWO-VARIABLE SYSTEMS

To illustrate the above analytic results for the stationary probability distribution in the vicinity of a limit cycle we choose a two-variable system. The deterministic dynamic equations are

$$\frac{dx_1}{dt}=A_1(x_1,x_2) , \tag{3.1}$$

$$\frac{dx_2}{dt}=A_2(x_1,x_2) . \tag{3.2}$$

Suppose this two-variable system has a stable limit cycle in the phase space (x_1,x_2). We define the new coordinate (ξ_1,ξ_2) such that ξ_1 is a distance along the attractor, that is the length of a path on the cycle, and ξ_2 is perpendicular to ξ_1. The unitary matrix of the transformation of variables is

$$B_{11}=\frac{A_1}{V} , \quad B_{12}=-\frac{A_2}{V} , \quad B_{21}=\frac{A_2}{V} , \quad B_{22}=\frac{A_1}{V}$$
$$\left[\sum_{k=1}^{2}B_{ik}B_{jk}=\delta_{ij}\right] . \tag{3.3}$$

The deterministic equations of motion for (ξ_1,ξ_2) are

$$\frac{d\xi_1}{dt}=V=\sqrt{A_1^2+A_2^2} , \tag{3.4}$$

$$\frac{d\xi_2}{dt}=-L\xi_2 , \quad L=L(\xi_1)=-\sum_{j,l}B_{j2}B_{l2}\frac{\partial A_j}{\partial x_l} . \tag{3.5}$$

The stationary probability density distribution of this two-variable system, in the limit $\Omega^{-1}\to 0$, is given by a stationary Fokker-Planck equation,

$$-\sum_i\frac{\partial}{\partial x_i}A_iP(x_1,x_2)+\sum_{i,j}\frac{\partial^2}{\partial x_i\partial x_j}D_{ij}P(x_1,x_2)=0 , \tag{3.6}$$

where the probability diffusion coefficients, D_{ij}, are of the order of Ω^{-1}, and may be state dependent or not.

As an example of a two-variable chemical system with a stable limit cycle, we consider the Selkov model,

$$R\underset{k_2}{\overset{k_1}{\rightleftarrows}}X , \quad X+2Y\underset{k_4}{\overset{k_3}{\rightleftarrows}}3Y , \quad Y\underset{k_6}{\overset{k_5}{\rightleftarrows}}P , \tag{3.7}$$

where R (P) denotes reactant (product) with a fixed concentration, X and Y are two intermediate chemical species, and k_i are rate coefficients of the reactions. We write x_1 and x_2 for the concentrations of species X and Y, and then the A_is on the rhs of Eqs. (3.1) and (3.2) are

$$A_1=k_1+k_4x_2^3-(k_2+k_3x_2^2)x_1 ,$$
$$A_2=k_6+k_3x_2^2x_1-(k_5+k_4x_2^2)x_2 . \tag{3.8}$$

For our example of chemical reaction in the Selkov model, Eq. (3.7), the stochastic description of the system, based on birth-death master equation, takes the form

$$\frac{dP(X,Y)}{dt}=\Omega k_1P(X-1,Y)+k_2(X+1)P(X+1,Y)+\frac{k_3}{\Omega^2}(X+1)(Y-1)(Y-2)P(X+1,Y-1)$$
$$+\frac{k_4}{\Omega^2}(Y+1)Y(Y-1)P(X-1,Y+1)+k_5(Y+1)P(X,Y+1)+\Omega k_6P(X,Y-1)$$
$$-\left[\Omega k_1+k_2X+\frac{k_3}{\Omega^2}XY^2+\frac{k_4}{\Omega^2}Y^3+k_5Y+\Omega k_6\right]P(X,Y) , \tag{3.9}$$

where X and Y are the numbers of X and Y molecules. Since we are only interested in the stationary density probability distribution, we set the right-hand side of this equation equal to zero. Rescaling the variables $x_1=X/\Omega$ and $x_2=Y/\Omega$, we obtain the stationary Fokker-Planck equation of the form of Eq. (3.6), with the probability diffusion coefficients

$$D_{11}=\frac{1}{2\Omega}[k_1+k_4x_2^3+(k_2+k_3x_2^2)x_1] ,$$
$$D_{22}=\frac{1}{2\Omega}[k_6+k_3x_2^2x_1+(k_5+k_4x_2^2)x_2] , \tag{3.10}$$
$$D_{12}=D_{21}=-\frac{1}{2\Omega}(k_3x_1x_2^2+k_4x_2^3) .$$

Rewriting Eq. (3.6) in terms of (ξ_1,ξ_2) coordinates, we have

$$-\left[\frac{\partial}{\partial x_i}A_i(\mathbf{x})\right]P(\xi)-V\frac{\partial}{\partial\xi_1}P(\xi)+\xi_2 L(\xi_1)P(\xi)+\sum_{i,j}(B^{-1})_{2i}(B^{-1})_{2j}D_{ij}(\xi)\frac{\partial^2}{\partial\xi_2^2}P(\xi)=0\ . \quad (3.11)$$

We seek the solution of Eq. (3.11), $P(\xi)$, in the form

$$P(\xi)=H(\xi_1)\exp[\Omega\gamma(\xi_1)\xi_2^2]\ , \quad (3.12)$$

where $H(\xi_1)$ and $\gamma(\xi_1)$ are to be determined. The equation for $\gamma(\xi_1)$ is given by Eq. (2.20); this is

$$V\frac{d\gamma}{d\xi_1}-2L(\xi_1)\gamma-2M(\xi_1)\gamma^2=0\ , \quad (3.13)$$

where $L(\xi_1)$ and $M(\xi_1)=2\Omega\sum_{i,j}B_{i2}B_{j2}\bar{D}_{ij}(\xi_1)$ are periodic functions of ξ_1, with the length of limit cycle $\oint d\xi_1$ as the period. The solution for $\gamma(\xi_1)$ periodic in ξ_1 follows from Eq. (3.13) (cf. also Appendix),

$$\frac{1}{\gamma(\xi_1)}=-2\int_0^{\xi_1}d\xi_1'\frac{M(\xi_1')}{V(\xi_1')}\exp\left[-2\int_{\xi_1'}^{\xi_1}d\xi_1''\frac{L(\xi_1'')}{V(\xi_1'')}\right]-\frac{2\exp\left[-2\int_0^{\xi_1}d\xi_1'\frac{L(\xi_1')}{V(\xi_1')}\right]}{1-\exp\left[-2\int_0^{L}d\xi_1'\frac{L(\xi_1')}{V(\xi_1')}\right]}\times\int_0^{L}d\xi_1'\frac{M(\xi_1')}{V(\xi_1')}\exp\left[-2\int_{\xi_1'}^{L}d\xi_1''\frac{L(\xi_1'')}{V(\xi_1'')}\right]\ . \quad (3.14)$$

Since both M and $\int_0^L d\xi_1' L(\xi_1')/V(\xi_1')$ are positive definite, $\gamma(\xi_1)$ is then negative definite, as expected for Gaussian fluctuations around a stable limit cycle. Equations (3.14), (2.26), and (2.33) define $H(\xi_1)$. Thus we have an explicit approximate solution for the probability distribution of a two-variable system in the vicinity of a stable limit cycle.

Equations (3.12) and (3.13) have much in common with the equations for the evolution of the probability density of a two-variable system with a limit cycle, which were considered in the Appendix of an interesting article [15]. The authors used the transformation to the variables normal and tangential to the cycle, as is done here. However, in the present paper, in contrast to [15], we analyze the *stationary* statistical distribution, and both the prefactor and the exponent in (3.12) are independent of time. The inequality $\int_0^L d\xi_1 L(\xi_1)V^{-1}(\xi_1)>0$ implemented in the present analysis is much less restrictive than $L(\xi_1)V^{-1}(\xi_1)>0$ imposed in [15].

IV. COMPARISON WITH NUMERICAL SOLUTIONS AND CONCLUSIONS

We calculated numerically by means of a Monte-Carlo method [16,17] the probability distribution for the Selkov model, from both the stationary Fokker-Planck equation, Eq. (3.6), with the probability diffusion coefficients Eq. (3.10), and the stationary master equation. If we take a master equation as an example, then the equation for the stationary distribution is of the form

$$\begin{aligned}&W\{(x+\Omega^{-1},y)\to(x,y)\}P(x+\Omega^{-1},y)+W\{(x-\Omega^{-1},y)\to(x,y)\}P(x-\Omega^{-1},y)\\&+W\{(x,y+\Omega^{-1})\to(x,y)\}P(x,y+\Omega^{-1})+W\{(x,y-\Omega^{-1})\to(x,y)\}P(x,y-\Omega^{-1})\\&+W\{(x+\Omega^{-1},y-\Omega^{-1})\to(x,y)\}P(x+\Omega^{-1},y-\Omega^{-1})+W\{(x-\Omega^{-1},y+\Omega^{-1})\to(x,y)\}P(x-\Omega^{-1},y+\Omega^{-1})\\&-P(x,y)(W\{(x,y)\to(x+\Omega^{-1},y)\}+W\{(x,y)\to(x-\Omega^{-1},y)\}+W\{(x,y)\to(x,y+\Omega^{-1})\}\\&+W\{(x,y)\to(x,y-\Omega^{-1})\}+W\{(x,y)\to(x+\Omega^{-1},y-\Omega^{-1})\}+W\{(x,y)\to(x-\Omega^{-1},y+\Omega^{-1})\})=0\ .\end{aligned} \quad (4.1)$$

An equivalent problem [16,17] is to trace the movement of such a random walker in x-y space: when this walker is at point (x,y) it can step randomly into its neighbors in six different directions $(x\pm1/\Omega,y)$, $(x,y\pm1/\Omega)$, and $(x\pm1/\Omega,y\mp1/\Omega)$ with probabilities $W(x,y\to x\pm1/\Omega,y)$, $W(x,y\to x,y\pm1/\Omega)$, and $W(x,y\to x\pm1/\Omega,y\mp1/\Omega)$, respectively. In the limit of large number of steps, the probability of a point (x,y) being visited by the random walker gives the solution of Eq. (4.1). The solution of a stationary Fokker-Planck equation can be found in a similar way.

The dimensionless volume of the system which scales the total number of particles, Ω, is chosen to be 50 000 in our calculation. For this volume size, the difference between the results from the master equation and that from the Fokker-Planck equation can hardly be observed at our resolution (200×200 grid). With the following values of parameters: $k_1=1.0$, $k_2=0.2$, $k_3=1.0$, $k_4=0.1$, $k_5=1.105$, and $k_6=0.1$, the Selkov model has a stable limit cycle, and the solution for the probability distribution is a volcano-shaped crater as depicted in Fig. 1, with the top of the crater corresponding to the location of the deterministic limit cycle. The top of the crater is uneven and the width of the crater varies from point to point.

In Fig. 2 we plot the probability distributions in a cross section transverse to the limit cycle obtained from numerical solution for the stationary distribution of the master equation, Eq. (4.1), and the analytic expression

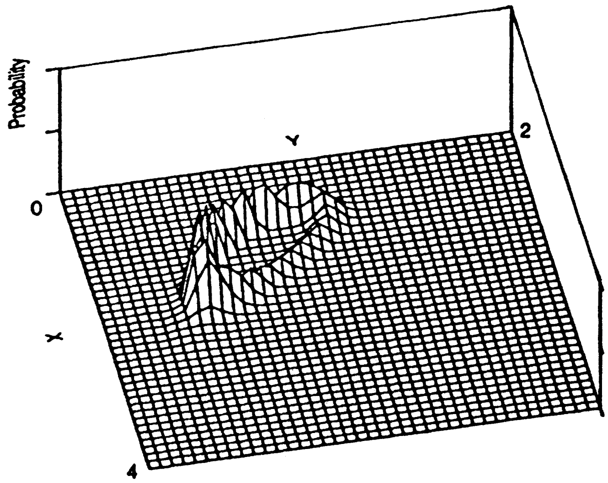

FIG. 1. Monte Carlo results for the stationary probability distribution for the Selkov model with the shape of a volcanic crater. The parameters are $k_1=1.0$, $k_2=0.2$, $k_3=1.0$, $k_4=0.1$, $k_5=1.105$, and $k_6=0.1$. The system has a stable deterministic limit cycle located on the ridge of the crater. The symbol Ω denotes the effective dimensionless volume which scales the total number of molecules, taken to be $\Omega=50\,000$.

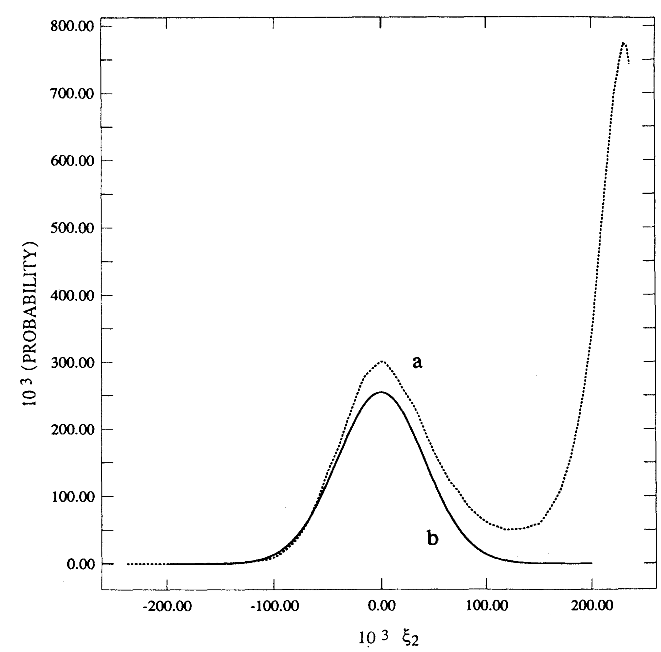

FIG. 2. The probability distributions in a cross section (transverse to the ridge) for the Selkov model. The parameters are the same as in Fig. 1. The on-cycle point, at which the cross section transverse to the limit cycle is taken, is $(x,y)=(1.894\,787, 0.690\,831\,5)$. (a) result of the Monte Carlo calculation of the stationary distribution of the master equation, Eq. (4.1); (b) analytic result from Eq. (3.12).

Eq. (3.12). The on-cycle point, where the cut of the cross section is taken, is $(x,y)=(1.894\,787, 0.690\,831\,5)$. The numerical solution is correct to only about 10%, mainly due to the finite time of the Monte Carlo simulation and the finite size of our example (of the order of 10^5 molecules). Within that range the analytic and numerical result agree quite well. The second peak of the plot from the Monte Carlo simulation, on the right-hand side of Fig. 2, is the ridge on the other side of the crater; the analytic solution yields only one peak everywhere on the limit cycle.

The data for H and γ as given by Eqs. (2.26) and (3.14) are plotted in Fig. 3. The requirements for a crater-shaped distribution from Eq. (3.12) that (i) both H and γ be periodic functions of ξ_1, with the length of the limit cycle as the period, (ii) $H>0$, and (iii) $\gamma<0$ are all satisfied.

In order to compare the height of the crater along the limit cycle, we plot in Fig. 4 H from Eq. (2.26) and the height of the crater along the limit cycle from the numerical simulation. We find these two curves match very well.

The area beneath the distribution surface $P(\xi_1,\xi_2)$ for a given ξ_1 is

$$\sigma(\xi_1)=\int_{-\infty}^{\infty}P(\xi_1,\xi_2)d\xi_2=\frac{H(\xi_1)\sqrt{\pi}}{\sqrt{-\Omega\gamma(\xi_1)}} . \tag{4.2}$$

The product of $\sigma(\xi_1)$ times the on-cycle speed $V(\xi_1)$ is predicted to be constant. The curve of $\sigma(\xi_1)V(\xi_1)$ from our analytic solution and numerical calculation in Fig. 4 supports this point.

In conclusion, we have constructed an explicit analytic solution of a Fokker-Planck equation, with small probability diffusion coefficient, in the vicinity of stable limit cycle. The distribution in the direction transverse to the limit cycle is Gaussian. The width and the height of this

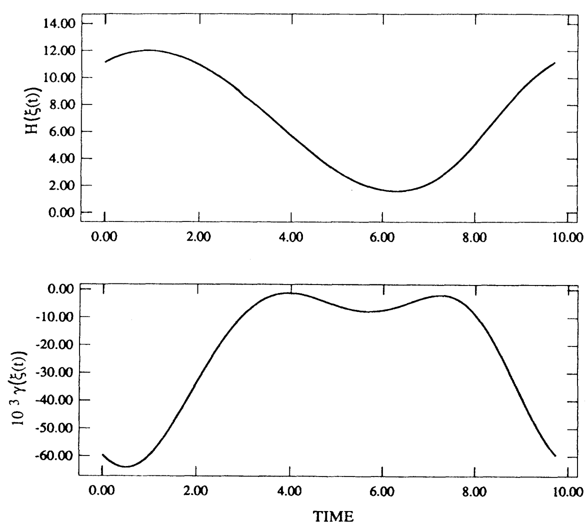

FIG. 3. H and γ as given by Eqs. (2.26) and (3.14) for the Selkov model vs time within a period of motion along the limit cycle. The parameters are the same as in Fig. 1. Time is related to ξ_1 via Eq. (2.5).

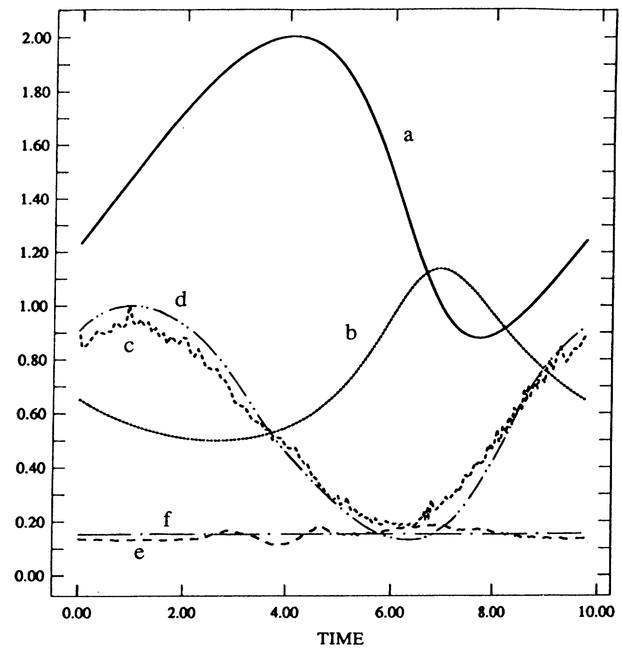

FIG. 4. Comparison of the analytic results with the numerical calculations for the Selkov model. The parameters are the same as in Fig. 1. Curve a: x, concentration of X, vs time; b: y, concentration of Y, vs time; curve c: numerical result: the height of the probability density in the cross section along the limit cycle with the maximum value normalized to unity; curve d: analytic result: same as curve c; curve e: numerical result: product of the area of the cross section times the velocity, which is almost constant, with some deviations due to the overlapping of the probability densities from two parts of the crater; curve f: analytic result: the product of the area of the cross section times the velocity.

distribution vary along the limit cycle. However the product of the area of the cross section times the velocity of the motion along the cycle remains constant. The Monte Carlo numerical simulation for a model oscillatory chemical system (Selkov model) has been performed, and the results are in good quantitative agreement with the theory. The result presented not only gives an analytic expression for the probability distribution near a limit cycle, it also paves the way to the solution of the more general problem of large fluctuations in systems without detailed balance that possess limit cycles, and of the fluctuational escape from such attractors.

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APPENDIX

The stationary solution to the Fokker-Planck equation of the form Eq. (2.15) makes sense provided the matrix $\hat{\gamma}$ is negative definite. It ensures that the probability distribution is Gaussian in the direction transverse to the limit cycle, with the maximum at the limit cycle. In order to prove this, we start from Eq. (2.9). We can define an operator $\hat{U}(t)=[U_{ij}(t)|i\geq 2, j\geq 2]$ such that

$$\xi_i(t)=\sum_{j\,(\geq 2)} U_{ij}(t)\xi_j(0) \quad (i\geq 2) . \tag{A1}$$

Substituting it into Eq. (2.9), we have

$$\hat{U}(t)=T\exp\left[-\int_0^t \hat{L}(\tau)d\tau\right] = \lim_{\Delta t\to 0} e^{-\hat{L}(t)\Delta t}e^{-\hat{L}(t-\Delta t)\Delta t}\cdots e^{-\hat{L}(\Delta t)\Delta t} , \tag{A2}$$

where T is the chronological ordering operator [the matrices $\hat{L}(\tau)$ for different instants τ do not commute with each other] and $\Delta t=\Delta\xi_1/V(\xi_1)$. The stability of the limit cycle requires that the deterministic trajectory approaches the limit cycle after a cycle; that is

$$\sum_{i\,(\geq 2)}\xi_i^2(t_p)<\sum_{i\,(\geq 2)}\xi_i^2(0) , \quad t_p=\int_0^L d\xi_1 V^{-1}(\xi_1) , \tag{A3}$$

where t_p is the period of the oscillation and L is the length of the limit cycle. Thus the absolute values of all the eigenvalues of the matrix $\hat{U}(t_p)$ must be less than 1; that is, if a canonical transformation that diagonalizes $\hat{U}(t_p)$ is $\hat{S}$,

$$[\hat{S}^{\dagger}\hat{U}(t_p)\hat{S}]_{ij}=u_i\delta_{ij} , \quad \hat{S}^{\dagger}\hat{S}=\hat{I} , \tag{A4}$$

then

$$|u_i|<1 . \tag{A5}$$

It is straightforward to show that Eq. (2.24) has a solution of the form

$$\hat{\gamma}^{-1}(t)=\hat{U}(t)\hat{\gamma}^{-1}(0)\hat{U}^{\dagger}(t)-\hat{U}(t)\hat{\mu}(t)\hat{U}^{\dagger}(t) , \tag{A6}$$

where

$$\hat{\mu}(t)=2\int_0^t d\tau\,\hat{U}^{-1}(\tau)\hat{M}(\tau)[\hat{U}^{\dagger}(\tau)]^{-1} . \tag{A7}$$

On application of periodic boundary conditions Eq. (2.25) to Eq. (A6) we have the equation for the matrix $\hat{\gamma}^{-1}(0)$,

$$\hat{\gamma}^{-1}(0)-\hat{U}(t_p)\hat{\gamma}^{-1}(0)\hat{U}^{\dagger}(t_p)=-\hat{U}(t_p)\hat{\mu}(t_p)\hat{U}^{\dagger}(t_p) . \tag{A8}$$

To solve this equation we multiply it by $\hat{S}^{\dagger}$ from the left-hand side and by $\hat{S}$ from the right-hand side, and then for the elements of the matrix,

$$\hat{g}=-\hat{S}^{\dagger}\hat{\gamma}^{-1}(0)\hat{S} , \tag{A9}$$

we obtain

$$g_{ij}=\frac{v_{ij}u_i u_j^*}{1-u_i u_j^*} , \tag{A10}$$

where

$$\hat{v}=\hat{S}^{\dagger}\hat{\mu}(t_p)\hat{S} . \tag{A11}$$

Since the matrix $\hat{M}(\tau)$ defined by Eq. (2.22) is symmetrical and positive definite (it is proportional to the matrix of the probability diffusion coefficients), the matrix

$$\hat{U}^{-1}(\tau)\hat{M}(\tau)[\hat{U}^{\dagger}(\tau)]^{-1}$$

is Hermitian and positive definite. Hence $\hat{\nu}$, which is obtained by integration and canonical transformation upon this matrix, is also Hermitian and positive definite. Therefore

$$\nu_{ii}>0\ ,\quad \nu_{ii}\nu_{jj}-\tfrac{1}{4}(\nu_{ij}+\nu_{ji})^2>0\ . \tag{A12}$$

It follows from (A10) and (A12), with account taken of Eq. (A5), that

$$g_{ii}>0\ ,\quad g_{ii}g_{jj}-\tfrac{1}{4}(g_{ij}+g_{ji})^2>0\ . \tag{A13}$$

Hence the matrix $\hat{g}$ is positive definite, and thus the matrix $\hat{\gamma}^{-1}(0)=-\hat{S}\hat{g}\hat{S}^{\dagger}$ is negative definite. Since the starting point $t=0$ on the limit cycle has been chosen arbitrarily, the matrix $\hat{\gamma}^{-1}(0)$ is negative definite everywhere on the cycle.

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