Statistical distribution and stochastic resonance in a periodically driven chemical system

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The probability density distribution is studied analytically and by Monte Carlo simulations for a periodically driven chemical bistable system, described by a master equation, for the case of low-frequency driving. The quasistationary distribution about the stable states is well approximated by the solution of the master equation in the eikonal approximation for large volumes of the system. For a one-component system both the exponent and the prefactor of the steady distribution are obtained in explicit form, for an arbitrary strength of the driving and for an arbitrary interrelation between the frequency of the driving and the probabilities of transitions between the stable states. The results of the simulations are in good agreement with analytical results. We demonstrate the onset of stochastic resonance for the driving frequency close to the probabilities of fluctuational transitions between the states. © *1995 American Institute of Physics.*

I. INTRODUCTION

The term ''stochastic resonance'' (SR) is used for a group of phenomena where the response of a system to a comparatively weak periodic input signal is enhanced by fluctuations, whether inherent to the system or imposed externally. Suggested initially[1] as a possible explanation of the ice ages, (SR) has attracted attention recently within a wide variety of contexts (see Refs. 2 and 3 for a review).

A simple model that displays SR and that has been investigated in most detail is a noise-driven bistable dynamical system. Noise gives rise to the fluctuational transitions $n \rightleftharpoons m$ between the stable states $(n,m=1,2)$. The dependence of the transition probabilities W_{nm} on the noise intensity is often of the activation type; in particular, for a system in thermal equilibrium we have $W_{nm} \propto \exp(-E_n/T)$ where E_n is the activation energy of escape from the state n and T is temperature in energy units. The distribution of the system over the stable states is formed on balance of the transitions, and the ratio of the populations of the states ν_1/ν_2 is $\propto \exp[(E_2-E_1)/T]$. If $E_2 \approx E_1$ the response of the system to a *low-frequency* periodic input signal may be strong, since the signal modulates the activation energies (e.g., the depths of the potential wells that correspond to the stable states); in its turn, this gives rise to the modulation of the populations of the states. The magnitude of the response is proportional to the difference between the values of the observed variable in the two stable states, and therefore it can be large even for a comparatively small signal. Clearly, the effect comes into play when the frequency of the signal $\omega \sim W_{12} \sim W_{21}$. The onset of a comparatively large response of this sort was considered by Debye[4] in the context of dielectric response due to reorientation of polar molecules among the equivalent states in a unit cell. More recently it was found that not only the signal at the output of the system, but even the signal-to-noise ratio at the output can strongly increase with the increasing noise intensity at the input.[5]

SR may be expected to occur as well in bistable chemical systems where the density x of a reagent takes on two stable values for given constraints, say the flux of the reactants into the system. Both the external fluctuations (e.g., due to the fluctuations in the density of the incoming flux, or in temperature) and the internal ones can give rise to the fluctuational transitions between the states (i.e., to the fluctuations of the molar volumes). An external periodic field can modulate the populations of the states, and the resulting response will be large in the region of the ''kinetic phase transition''[6] where the populations are close to each other (we use the term ''population of the state,'' in chemical context, in the same meaning as it is used in the context of dynamical systems: the probability to find the system in the stable state, not the number of species in this state).

We are interested in internal fluctuations due to the finite number of the molecules of the reagents. Such fluctuations are of particular interest for small reactors like cellular vesicles.[7] The dependence of the switching probabilities on the average number of reacting molecules N, or on the volume of the system V $(N \propto V)$, is exponential (see Ref. 8, and also Ref. 9), $W_{nm} \propto \exp(-Vs_n)$ where s_n depends on the densities of the reagents and is independent of the volume, in the limit of large N. It is the volume, or the number of molecules in the system, that play here the role of the reciprocal noise intensity in noise-driven dynamical systems. Interesting results on SR in a spatially uniform chemical system were obtained numerically by Leonard and Reichl,[10] and we shall discuss these later.

In the present paper we investigate steady periodic probability distribution of a periodically driven bistable chemical system described by a master equation. We provide an *explicit analytic solution* to this long-standing problem in the case of low-frequency driving, *without* imposing a limitation that the driving be weak (which is commonly used in the

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theory of SR). We compare the results with the results of extensive Monte Carlo simulations. We demonstrate the onset of SR in the region where the populations of the stable states are of the same order of magnitude and where the probabilities of the transitions are of the same order as the driving frequency.

II. EIKONAL APPROXIMATION TO THE SOLUTION OF MASTER EQUATION

For simplicity we consider a situation where there is only one variable reagent in a spatially homogeneous reactor, with the number of molecules X, as is the case in the Schlögl model, e.g., Ref. 11. This number changes as a result of the collisions that give rise to the reactions. The collisions happen at random, and therefore for low densities the quantity $X(t)$ is a Markovian random process; its probability density $P(X,t)$ is described by a master equation (a birth–death equation),

$$\frac{\partial}{\partial t}P(X,t)=\sum_{r=\pm 1,\pm 2,\ldots,}[W(X-r,r;\theta)P(X-r,t) - W(X,r;\theta)P(X,t)], \quad \theta=\omega t, \tag{1}$$

where $W(X,r;\theta)$ is the probability per unit time of the reaction $X\rightarrow X+r$ in which the number of the molecules X increases by r. The quantity $\theta\equiv\omega t$ is the phase of the external field that periodically modulates the density of the incoming species, or temperature, etc. We assume that the reaction probabilities are periodic in θ,

$$W(X,r;\theta+2\pi)=W(X,r;\theta). \tag{2}$$

In the limit of large volume V (large numbers X) the reaction probabilities $W(X,r;\theta)$ obey the scaling

$$W(X,r;\theta)/V=w(x,r;\theta)+o(V^0), \quad x=X/V. \tag{3}$$

Here, x is the density of the species we investigate, and $w(x,r;\theta)$ is the reaction probability density per unit volume; it is independent of V.

The distribution $P(X,t)$ peaks sharply at the average number of molecules $\bar{X}(t)$, with the characteristic width $\sim\bar{X}^{1/2}\ll\bar{X}$.[12] The time evolution of $\bar{X}(t)$ and of the average density $\bar{x}(t)\equiv\bar{X}(t)/V$ with the neglect of fluctuations, is described by the rate equation that follows from Eq. (1) if one assumes that the probabilities $W(X,r;\theta)$ are smooth as functions of X and their dependence on X may be neglected within the range where $P(X,t)$ is large. We have

$$d\bar{X}/dt\equiv\sum_X X\,[dP(X,t)/dt]\approx\sum_r rW(\bar{X},r;\theta),$$
$$d\bar{x}/dt\approx\sum_r rw(\bar{x},r;\theta). \tag{4}$$

If a system is bistable in the absence of periodic driving, Eqs. (4) have two stable stationary solutions for the density $\bar{x}$: $\bar{x}=x_1$ and $\bar{x}=x_2$. In the presence of driving, where the functions w explicitly depend on time, the stationary stable solutions of Eqs. (4) are, generally speaking, periodic, and in the simplest case with the same period as the driving, $x_n\equiv x_n(\theta)=x_n(\theta+2\pi)$ (SR in a dynamical system that displays period doubling has been considered in Ref. 13). A characteristic "dynamical" relaxation time t_r within which the system approaches a stationary state may be found from Eqs. (4) linearized about this state,

$$t_r=\max\left|\frac{\partial}{\partial x}\sum_r rw(x,r;\theta)\right|_{x_n}^{-1}.$$

It follows from Eqs. (4) that t_r is independent of the volume of the system.

The stationary solution of the master equation (1) $P_{\rm st}(X,t)$ is periodic, with the period $2\pi/\omega$: $P_{\rm st}(X,t)=P_{\rm st}(X,t+2\pi\omega^{-1})$. This solution, in the case of a bistable system, is formed in two stages: first, over the time t_r there are formed quasistationary periodic distributions $P_n(X,t)$ about the stable periodic states $X_n(t)$,

$$P_n(X,t)=P_n\left(X,t+\frac{2\pi}{\omega}\right) \tag{5}$$

and then, over a much longer time which is determined by the probabilities W_{nm} of the fluctuational transitions between the states, there is formed the global distribution $P_{\rm st}(X,t)$.

The quasistationary solution of Eq. (1) in the case of a large number of molecules X can be sought in the form of eikonal approximation—the approach that has proven to provide good results in the absence of periodic driving, including the case of systems lacking detailed balance (see Ref. 9 and references therein).

We formally rewrite the master equation (1) for the quasistationary distribution $P_n(X,t)$ in the differential form (cf. Ref. 14)

$$\frac{\partial}{\partial t}P_n(X,t)=\sum_r(e^{-r\partial/\partial X}-1)W(X,r;\theta)P_n(X,t),$$
$$P_n(X,t)=\exp[-S_n(X,t)]. \tag{6}$$

The function $S_n(X,t)$ is proportional to the volume of the system V, and the derivatives of S_n over X ($X\propto V$) are independent of the volume, whereas $(\partial/\partial X)\ln W(X,r;\theta)\propto 1/V$. Therefore to the lowest order in V^{-1} we arrive at the following equation for the eikonal S_n/V:

$$\frac{\partial s_n}{\partial t}+H\left(x,\frac{\partial s_n}{\partial x};\theta\right)=0, \quad s_n\equiv s_n(x,t)=V^{-1}S_n(X,t).$$
$$H(x,p;\theta)=\sum_r w(x,r;\theta)(e^{rp}-1). \tag{7}$$

The approximations (6) and (7) do not apply in the vicinity of the *unstable* stationary solution of Eqs. (4), as it is clear from the above consideration of the times that characterize the kinetics: Eqs. (6) and (7) do not allow for exponentially large relaxation times, and the number of species has dropped out of the equation for s_n. This is why we consider the eikonal solution for the *quasistationary* distribution P_n rather than to seek directly the stationary distribution $P_{\rm st}$ throughout the space of the variable X.

Equation (7) is of the form of an Hamilton–Jacobi equation for an auxiliary dynamical system with a Hamiltonian H that periodically depends on time; the function $s_n(x,t)$ is the action of this system. Since we are interested in the solution for P_n that is periodic [cf. Eq. (5)], we have

$$s_n(x,t+2\pi\omega^{-1})=s_n(x,t). \tag{8}$$

The function $s_n(x,t)$ has a *minimum* at the value of the density $x(t)$ that corresponds to the stable stationary periodic state of the system, $x(t)=\bar{x}_n(t)$, and s_n is parabolic (in x) near the minimum, with the curvature varying periodically in time. In solving Eqs. (7) and (8) we have to allow for the fact that the auxiliary dynamical system (7) is nonintegrable, as is also true in the analysis of large fluctuations in continuous systems driven by white noise.[15] Therefore the paths of this system $x(t)$ encounter caustics and display a complicated behavior. However, it may be shown[16] that the paths that are of physical significance for the initial problem of the fluctuating system (1), (5) do not encounter caustics, as in the case of a many-variable fluctuating system without periodic driving.[17]

III. LOW-FREQUENCY DRIVING

A. Quasistationary distribution about the stable states

Interesting effects related to the fluctuation-mediated periodic redistribution of the system over the stable states may be expected in the range of frequencies $\omega\sim W_{nm}\ll t_r^{-1}$. In this range the local behavior of the system in the vicinity of a stable state follows the driving *adiabatically*, without retardation: the position of the state x_n and the shape of the quasistationary distribution $P_n(X,t)$ are determined by the *instantaneous* value of the phase of the driving θ. In contrast, the redistribution over the states occurs over the time $\sim W_{nm}^{-1}\sim\omega^{-1}$, and therefore in evaluating the time dependence of the populations of the states ν_n it is necessary to allow for the fact that the transition rates W_{nm} vary in time on the time scale ω^{-1}.

These arguments suggest that we may seek the quasistationary distribution in the form

$$\begin{aligned}
&P_n(X,t)=\nu_n(t)\left[\frac{V}{2\pi}\,s_n''(x_n;\theta)\right]^{1/2}\exp\{-Vs_n(x;\theta)\},\\
&\qquad x_n\equiv x_n(\theta),\quad \theta=\omega t,\\
&H\left(x,\frac{\partial s_n(x;\theta)}{\partial x};\theta\right)=0,\quad s_n(x_n;\theta)=0,\\
&\left[\frac{\partial}{\partial p}\,H(x_n,p;\theta)\right]_{p=0}=0\\
&s_n''(x_n;\theta)\equiv\left[\frac{\partial^2 s_n(x;\theta)}{\partial x^2}\right]_{x_n(\theta)}=-2\left[\sum_r r\,\frac{\partial w(x,r;\theta)}{\partial x}\right]_{x_n}\\
&\qquad\times\left[\sum_r r^2 w(x_n,r;\theta)\right]^{-1}.
\end{aligned} \tag{9}$$

According to our adiabatic picture we have dropped the derivative $\partial s_n/\partial t\sim\omega s_n$ present in Eq. (7), and we thus arrive at the "time-independent" Hamiltonian H for the conservative motion of an auxiliary system with the energy equal to zero. The equation $\partial H/\partial p=0$ for $p=0$ defines the position of the stable state x_n. This position varies parametrically with θ, and the equation coincides with the corresponding equation that follows from Eqs. (4) if one neglects $d\bar{x}/dt\sim\omega\bar{x}$.

It is clear from (7) that Eq. (9) for s_n' is just an algebraic equation in the one-variable case considered. The explicit solution of it can be found for some simple models of $w(x,r)$ (cf. Refs. 8 and 18); it has a particularly simple form near the stable state:

$$s_n(x;\theta)\approx\tfrac{1}{2}\,s_n''(x_n;\theta)(x-x_n)^2\quad\text{for } |x-x_n|\ll|x_1-x_2|, \tag{10}$$

where s_n'' is given explicitly in Eqs. (9).

The transitions between the stable states occur when a system, as a result of a fluctuation, goes from one state to another over the unstable stationary state (saddle point) $x_s(\theta)$ that lies between the states x_1 and x_2. In what follows we assume

$$x_1<x_s<x_2.$$

For Markovian systems the probability W_{nm} of the escape from the state n is given, to logarithmic accuracy, by the probability to reach the unstable stationary state point, i.e., in the considered case, by the value $s_n(x_s;\theta)$ of the action in the state x_s. The probability $W_{nm}\equiv W_{nm}(\theta)$ is a periodic function of θ, and thus of time, and the equation for the populations (mole fractions) of the stable states

$$\begin{aligned}
&\frac{d\nu_1}{dt}=-[W_{12}(\theta)+W_{21}(\theta)]\nu_1+W_{21}(\theta),\\
&\nu_2=1-\nu_1,\quad W_{nm}(\theta)=W_{nm}(\theta+2\pi)
\end{aligned} \tag{11}$$

has a periodic solution, as explained in Sec. I. The amplitude of the oscillations of $\nu_{1,2}$ depends on the interrelation between the values of ω and W_{nm}. For a high-frequency driving or for very small fluctuation intensity, where $\omega\gg W_{12}+W_{21}$, the populations $\nu_{1,2}$ remain nearly constant,

$$\nu_1\simeq\frac{\bar{W}_{21}}{\bar{W}_{12}+\bar{W}_{21}},\quad \bar{W}_{nm}=\frac{1}{2\pi}\int_0^{2\pi}d\theta W_{nm}(\theta).$$

On the contrary, if the transition probabilities W_{12}, W_{21} are of the same order of magnitude as the driving frequency ω, then the modulation of the populations ν_1, ν_2 in time is as strong as the modulation of the transition probabilities themselves. This demonstrates that by increasing fluctuations (by reducing the number of molecules) it is possible to increase the response to the periodic driving—which is the basic feature of stochastic resonance.

B. Transition probabilities

In the case of slowly varying driving it is possible to find not only the exponent, but also the prefactor in the expression for the transition probability. We shall illustrate this with

W_{12} taken as an example. To find W_{12} we assume that the state 1 ($x_1<x_s$) is occupied initially, whereas the state 2 is empty. Over the time $\sim t_r$ there is formed a quasistationary flux from the state 1 to the state 2 over the unstable stationary state x_s. In the vicinity of x_s the quasistationary solution of the master equation that describes this quasistationary flux is of the form

$$P_1(X,t)=C_1\ \exp\{-Vs_1(x_s;\theta)\}\int_x^\infty dy \times\exp\{-\tfrac{1}{2}\,Vs''(x_s;\theta)[(x-x_s)^2-(y-x_s)^2]\},\quad |x-x_s|\ll|x_1-x_s|, \tag{12}$$

$$s''(x_s;\theta)=-2\left[\sum_r\ r\,\frac{\partial w(x,r;\theta)}{\partial x}\right]_{x_s}\left[\sum_r\ r^2w(x_s,r;\theta)\right]^{-1};\qquad s''(x_s;\theta)<0.$$

The last inequality follows from Eqs. (4) if one allows for the fact that x_s is the unstable stationary solution for $\bar{x}$; the quantity $s''(x_s;\theta)\equiv s_1''(x_s;\theta)\equiv s_2''(x_s;\theta)$ is determined by the local values of the coefficients $w(x_s,r;\theta)$ and their derivatives, and therefore is the same for s evaluated for the state 1 or the state 2. The constant C_1 can be easily found by matching the solution (12) to the solution (9) in the range $x_s-x_1\gg x_s-x\gg V^{-1/2}$.

To express the flux out of the state 1 in terms of P_1 we put Eqs. (12) into the master equation (6) and integrate the latter over X from $-\infty$ to a given X close to X_s. For the normalization of P_1 chosen in Eqs. (9) the left-hand side of Eq. (6) transforms, upon integration, into $V\,d\nu_1/dt$, whereas the right-hand side, to the lowest order in V^{-1}, becomes equal to the flux into the state 1:

$$V\frac{d\nu_1}{dt}=-J_1;$$

$$J_1=J_1(x)=-\int_{-\infty}^{X}dX\ \sum_r\ (e^{-r\partial/\partial X}-1)W(X,r;\theta)P_1(X,t)\approx\frac{1}{2}\,C_1\ \exp\{-Vs_1(x_s;\theta)\}\sum_r\ r^2w(x_s,r;\theta) \tag{13}$$

[we have used here the explicit form of the action s_1 near the saddle point and allowed for the fact that for $x\approx x_s$ we have $\Sigma_r rw(x,r;\theta)\approx(x-x_s)\Sigma_r r[\partial w(x,r;\theta)/\partial x]$ where the derivative is evaluated for $x=x_s$]. It follows from the above expression that the flux J_1 as given by Eq. (13) is *independent* of x near the saddle point—particles are not accumulated in the vicinity of x_s. The ratio of the flux density J_1/V to the population ν_1 of the stable state 1 is equal to the transition probability W_{12}, and we get

$$W_{nm}(\theta)=\frac{1}{4\pi}\left[\sum_r\ r^2w(x_s,r;\theta)\right]\times\{s_n''(x_n;\theta)|s''(x_s;\theta)|\}^{1/2}\exp[-Vs_n(x_s;\theta)] \tag{14}$$

(the answer is written for the general case of the probability of the $n\to m$ transition).

C. Global distribution

We are now in a position to find not only the local shape of the quasistationary distribution, but also the global periodic distribution of the system in explicit form. This distribution has two basic constituents: (i) the local distributions about the states 1,2 which are given by Eqs. (9), with the populations of the states ν_1,ν_2 given by the balance Eqs. (11), and (ii) the term that describes the flux between the states which is formed on balance of the fluxes (13) from each of the states. It is clear from Eqs. (12) and (13) that this term is substantial in the vicinity of the saddle point [where the distributions (9) are small]; it can be written as

$$P_{\rm fl}(X,t)=C_{\rm fl}(t)\int_x^{x_s}dy\times\exp\{-\tfrac{1}{2}\,Vs''(x_s;\theta)[(x-x_s)^2-(y-x_s)^2]\},\quad |x-x_s|\ll|x_{1,2}-x_s|. \tag{15}$$

The flux J as given by Eq. (13), with $P_1(X,t)$ replaced by $P_{\rm fl}(X,t)$, is independent of the coordinate x (as it should be in the quasistationary case). The constant $C_{\rm fl}$ can be found from the fact that this flux is equal to $J=\frac{1}{2}\times C_{\rm fl}(t)\Sigma_r r^2w(x_s,r;\theta)\equiv -V\dot{\nu}_1\equiv V\dot{\nu}_2$. Taking Eqs. (9) and (14) into account one gets

$$C_{\rm fl}(t)=\frac{V}{2\pi}|s''(x_s;\theta)|^{1/2}\times\{[s_1''(x_1;\theta)]^{1/2}\exp[-Vs_1(x_s;\theta)]\nu_1(t)-[s_2''(x_2;\theta)]^{1/2}\exp[-Vs_2(x_s;\theta)]\nu_2(t)\}. \tag{16}$$

The function $P_{\rm fl}$ increases exponentially fast away from the saddle point. The form of $P_{\rm fl}(X,t)$ is Gaussian, i.e., the same as that of $\exp[-Vs_{1,2}(x;\theta)]$ near x_s. The expression for $P_{\rm fl}(X,t)$ can be written as

$$P_{\rm fl}(X,t)=\begin{cases}C_{\rm fl}(t)\displaystyle\int_x^{x_s}dy\ \exp\{-V[s_1(x;\theta)-s_1(x_s;\theta)-\tfrac{1}{2}(y-y_s)^2s''(x_s;\theta)]\}, & x\leqslant x_s\\ C_{\rm fl}(t)\displaystyle\int_x^{x_s}dy\ \exp\{-V[s_2(x;\theta)-s_2(x_s;\theta)-\tfrac{1}{2}(y-y_s)^2s''(x_s;\theta)]\}, & x\geqslant x_s\end{cases}.$$

Far from the saddle point the two expressions on the right-hand side can be written as

$$(-1)^{n-1}\tfrac{1}{2}[2\pi/V|s''(x_s;\theta)|]^{1/2}C_{\rm fl}(t)$$
$$\times\exp\{-V[s_n(x;\theta)-s_n(x_s;\theta)]\},\quad n=1,2.$$

The corresponding terms should be compensated in the vicinity of the attractors, since the distribution there is given by Eqs. (9) and (11). The compensating terms can be found if we notice that the master equation is linear, and so any combination of the solutions is a solution as well; therefore the appropriately weighted terms $\exp\{-Vs_{1,2}(x;\theta)\}$ can be just added to $P_{1,2}(X,t)$ in addition to $P_{\rm fl}(X,t)$, and they will not affect the flux between the states. With account taken of the explicit form of the coefficient $C_{\rm fl}(t)$ we arrive at the following expression for the statistical distribution:

$$P(X,t)=P_{\rm fl}(X,t)\frac{1}{2}\left(\frac{V}{2\pi}\right)^{1/2}\exp\{-Vs_n(x;\theta)\}$$
$$\times\{\nu_n(t)[s_n''(x_n;\theta)]^{1/2}+\nu_{3-n}(t)$$
$$\times[s_{3-n}''(x_{3-n};\theta)]^{1/2}$$
$$\times\exp[Vs_n(x_s;\theta)-Vs_{3-n}(x_s;\theta)]\},\qquad(17)$$

where

$$n=1\quad\text{for}\quad x\leqslant x_s,\quad n=2\quad\text{for}\quad x\geqslant x_s;$$
$$x_n\equiv x_n(\theta),\quad x_s\equiv x_s(\theta);\quad \theta=\omega t.$$

Equation (17) provides a complete global quasistationary probability distribution for a periodically driven system in the case of slowly varying driving. It has the right asymptotics (9) near the stable states and describes the flux between the states. We emphasize that we have not assumed that the driving is to any extent weak—the only assumption made was that it was slow compared to the relaxation of the system towards a stable steady state. We notice that the distribution (17) is continuous across the saddle point. At the same time, it is noticeably different from the corresponding solution in the stationary situation. In this latter case $\nu_1/\nu_2=W_{21}/W_{12}$, and thus $C_{\rm fl}=0$, so, the flux term $P_{\rm fl}(X,t)$ is absent (not surprisingly); at the same time, the intrawell solutions (9) match each other in the saddle point. In the next section we give the results of the Monte Carlo simulation of a chemical system and compare them with the analytical results obtained above, applied to the same model.

IV. MONTE CARLO SIMULATION OF PERIODICALLY DRIVEN SCHLÖGL MODEL

We consider a chemical reaction with the mechanism

$$A+(m-1)X\underset{k_2}{\overset{k_1}{\rightleftharpoons}}mX,\quad X\underset{k_4}{\overset{k_3}{\rightleftharpoons}}B\qquad(18)$$

in a reactor of volume V, where the numbers of molecules of species A and B are assumed to be controlled externally. If $m=3$, this is the Schlögl model,[11] and it may display bistability. Under appropriate assumptions the kinetics of the system is described by a birth–death master equation (cf. Refs. 8 and 19). By denoting the numbers of molecules of species X, A, and B by the same symbols we may write this equation in the form (1), with

$$W(X,1;\theta)=k_1V^{-m+1}AX!/(X-m+1)!+k_4B,$$
$$W(X,-1;\theta)=k_2V^{-m+1}X!/(X-m)!+k_3X.\qquad(19)$$

The functions $W(X,\pm1;\theta)$ depend on time via (one of) the externally controlled densities A or B, e.g., which are assumed to be periodic functions of $\theta=\omega t$.

We have performed Monte Carlo (MC) simulation of the system (18) and (19) with $m=3$, $k_1=k_2=k_3=k_4=1$, $A=1.9$ V, and with the number of species $B=(0.14+0.01\sin\theta)V$ periodically varying in time. The calculations were done using Gillespie's method[20] appropriately modified for driven systems. The number of Monte Carlo steps taken per each run is 10^9. For the chosen values of the parameters, and for the amplitude of the modulation set equal to zero, the system is bistable in the limit $V\to\infty$; the characteristic relaxation time $t_r\sim1$. For this set of the parameters, and again in the absence of the modulation, the populations of the stable states with smaller and larger density $x=X/V$ are close in order of magnitude.

MC has been performed for the effective volumes of the system $V=$ 400, 300, and 200 (the value of V characterizes the total amount of X molecules in the system). For the above V, the rates of the transitions between the states are $W\equiv W_{12}+W_{21}\simeq0.0007$, 0.0023, 0.0075, respectively. The MC demonstrates the double-peaked distribution $P(X)$, with the positions of the peaks x_1,x_2 given to a good accuracy by the stable stationary solutions of Eqs. (4).

In the presence of low-frequency driving the double-peaked structure of the stationary periodic distribution persists, but the heights (the intensities) of the peaks vary in time due to the periodic redistribution of the system over the stable states. The evolution of the distribution with the varying phase of the driving $\theta=\omega t$ is demonstrated in Fig. 1 for a few values of the volume V. As expected, the redistribution

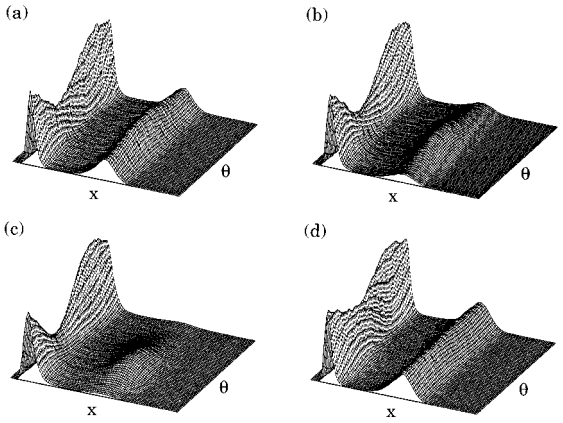

FIG. 1. Monte Carlo results on the dependence of the distribution as given by Eqs. (1) and (19) on the phase θ of the periodic driving in the range of the densities $0<x\equiv X/V<2$. The plots refer to the following parameter values: (a) $V=400,\omega=0.01$; (b) $V=300,\omega=0.01$; (c) $V=200,\omega=0.01$; and (d) $V=400,\omega=0.1$.

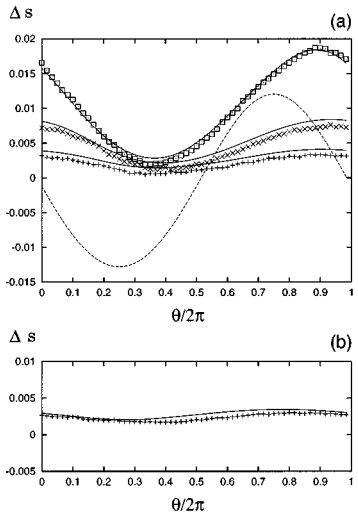

FIG. 2. The logarithm of the ratio of the heights of the distribution in the stable states vs the phase of the driving for (a) $V=400$ (pluses), 300 (crosses), and 200 (squares) with $\omega=0.01$ and (b) $V=400$ with $\omega=0.1$. The solid lines is the theory (17), the dashed line shows the limiting result of $\omega\to 0$.

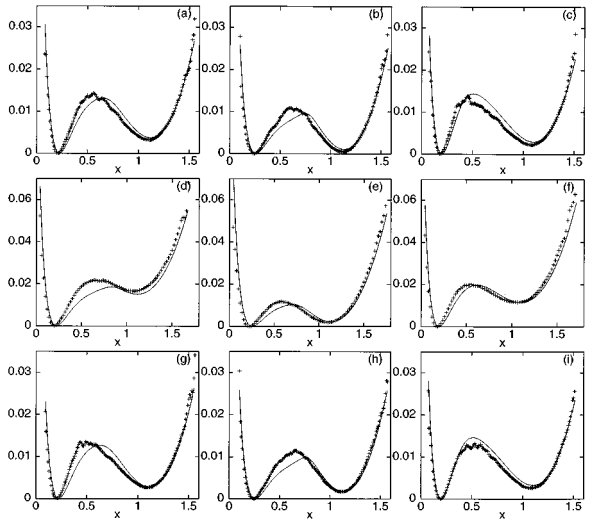

FIG. 3. The logarithm of the distribution. Pluses: Monte Carlo data; solid lines: the normalized logarithm of the global quasistationary distribution (17). The values of V and ω are $V=400,\omega=0.01$ in (a), (b), and (c), $V=200,\omega=0.01$ in (d), (e), and (f), and $V=400,\omega=0.1$ in (g), (h), and (i). The values of θ are 0 in (a), (d), and (g), $\pi/3$ in (b), (e), and (h), and $2\pi/3$ in (c), (f), and (i).

of the system over the stable states becomes more and more pronounced as the transition rate W approaches the driving frequency ω [Figs. 1(a)–1(c)]. On the contrary, if the frequency is very much higher than the transition probabilities, $\omega \gg W_{12}+W_{21}$, the redistribution over the states is weak, as it is seen from Fig. 1(d). These results are in qualitative agreement with the results by Leonard and Reichl[10] obtained by solving numerically the master equation for the reaction $A+2X\rightleftharpoons 3X$, $B+X\rightleftharpoons C$.

We emphasize that in the appropriate range of ω the strong redistribution of the system over the stable states is observed in response to driving with an extremely small amplitude, which is a clear indication of the onset of stochastic resonance. The redistribution is further seen in Fig. 2 where the logarithm of the *ratio* of the distribution $P(X,t)$ in its maxima at $X_2\equiv Vx_2$ and $X_1\equiv Vx_1$ $(X_2>X_1)$ is plotted *vs* the phase of the driving θ:

$$\Delta s(\theta)\equiv s(x_2;\theta)-s(x_1;\theta)=V^{-1}\ \ln[P(X_1,t)/P(X_2,t)]. \tag{20}$$

It is seen from Fig. 2 that the MC results obtained for the frequencies $\omega \ll t_r^{-1}$ are in good agreement with the theoretical results obtained in adiabatic approximation from Eqs. (9) [that relate $P(X,t)$ to the populations of the stable states $\nu_{1,2}$] and Eqs. (11) for the populations $\nu_{1,2}(t)$ themselves [we took the periodic solution of Eqs. (11) for the populations]. The agreement is good throughout the whole range of the volumes V and the frequencies ω investigated. The comparison with the theory is facilitated by the fact that, for the reaction considered, the explicit solution of Eq. (9) for the logarithm of the distribution is known:[19]

$$s_n(x;\theta)=\int_{x_n}^{x} dx'\ \ln\left[\frac{w(x',-1;\theta)}{w(x',1;\theta)}\right]. \tag{21}$$

In Fig. 3 we present the MC results for the shape of the *global* distribution at a few values of the phase of the driving and compare them with the theoretical expression (17). The agreement is good for all the phases and for all frequencies and volumes investigated. We emphasize that the theory does not contain any adjustible parameters.

V. CONCLUSIONS

It follows from the above results that the probability density distribution in a periodically driven spatially uniform chemical system may be well described in the eikonal approximation for a large enough number of molecules, both locally (within a range of attraction to each stable state) and globally. In the eikonal approximation the problem of large fluctuations is reduced to the problem of dynamics of an auxiliary periodically driven dynamical system. For a system with one variable reagent the latter problem can be solved in explicit form in the limiting case of driving at frequencies that are small compared to the reciprocal relaxation time of the chemical system in the absence of fluctuations. Both the logarithm and the prefactor in the probability density distribution and in the probabilities of transitions between coexisting stable states can be obtained. The analytical results obtained for a bistable system driven at low frequency and the data of Monte Carlo simulations demonstrate the onset of stochastic resonance: by reducing the number of molecules, and thus by increasing fluctuations, it is possible to get a large response to a small-amplitude driving. Similar to what happens in fluctuating dynamical systems [1,2] the response is large when the driving frequency is of the same order of magnitude as the probabiities of the transitions between the stable states.

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