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BRIEF REPORTS

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Stochastic resonance in a chemical reaction

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As a prototypical autocatalytic reaction, we study the Schlögl reaction scheme: $A+2X \rightleftharpoons 3X$, $B+X \rightleftharpoons C$. We focus on the population of species X, and describe the process through a birth-death master equation to retain the effects of internal fluctuations. We show that in the bistable regime, internal fluctuations can strongly amplify the system's response to weak, harmonic fields. The mechanism is a stochastic resonance in which the source of noise is the internal dynamics rather than a random environment.

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I. INTRODUCTION

Benzi, Sutera, and Vulpiani introduced an important phenomenon, which they named stochastic resonance, to explain the 100 000-year periodicity of the ice ages [1,2]. They showed how random environmental fluctuations can strongly amplify a small periodic force in a bistable system. In short, the presence of noise allows coherent, interwell transitions in an otherwise trapped, deterministic system. Consequently, small, intrawell oscillations become large, interwell jumps. Until this discovery, the 100 000-year variation in the eccentricity of Earth's orbit was considered much too small an influence to effect such extreme climate shifts. Today, this type of behavior continues to receive much attention both as a topic of general interest and in a variety of specific systems subjected to periodic forcing and random noise. Among these are electronic switching circuits [3], the bidirectional ring laser [4], electron-paramagnetic-resonance systems [5], and signal processing in neural systems [6]. It has been suggested as the mechanism for small-signal detection [7]. In all these systems, noise can be considered an external input. In this Brief Report, we show that such behavior is also exhibited by a chemical-reaction model in which the only source of fluctuations is the internal degrees of freedom.

In Secs. II and III we define the birth-death master equation that defines our model and choose appropriate parameters for observing stochastic resonance. In Secs. IV and V we investigate numerical solutions and realizations, respectively, of the master equation. Section VI concludes and suggests extensions in which we are interested.

II. MASTER EQUATION FOR DRIVEN SCHLÖGL MODEL

We choose an autocatalytic scheme because that is the simplest mechanism leading to multistability. There are many examples of multistable reactions that have been observed experimentally (see, e.g., Ref. [8]). The mechanisms of these reactions are typically high dimensional and therefore intractable from an analytic point of view. As an attempt to demonstrate stochastic resonance in such a setting, we choose a highly simplified, one-dimensional scheme: Schlögl's nonlinear chemical reaction [9],

$$A+2X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3X \; , \tag{2.1a}$$

$$B+X \underset{k_4}{\overset{k_3}{\rightleftharpoons}} C \; . \tag{2.1b}$$

In order to retain the effect of chemical fluctuations, we describe the time evolution of the probability for a population number n of species X by a birth-death master equation

$$\frac{d}{dt}P_n(t)=t_{n-1}^{+}(t)P_{n-1}(t)+t_{n+1}^{-}(t)P_{n+1}(t) -[t_n^{+}(t)+t_n^{-}(t)]P_n(t) \; . \tag{2.2}$$

The transition probabilities per unit time are

$$t_n^{+}(t)=\alpha n(n-1)+\gamma(t) \; , \tag{2.3a}$$

$$t_n^{-}=n(n-1)(n-2)+\beta n \; , \tag{2.3b}$$

with dimensionless parameters $\alpha=k_1[A]V/k_2$, $\beta=k_3[B]V^2/k_2$, $\gamma=k_4[C]V^3/k_2$. Time is made dimensionless by multiplying by the rate k_2/V^2. V is the volume of the reaction cell. The parameter γ contains an oscillatory part, $\gamma(t)=\gamma_0+\epsilon\cos(2\pi f_0 t)$, due to external harmonic forcing which amounts to pumping the species C into the cell harmonically. The system is assumed to be spatially homogeneous.

The process described by the master equation, Eq. (2.2), can be visualized as a random walk in continuous time in which the one-step right and left transition probabilities are not equal but reflect the slope of the time-dependent stochastic potential. Recently, a master equation modeling a pure random walk with additive bias in the transition probabilities was shown to exhibit stochastic resonance [10]. In that case, however, the relative strength of fluctuations was an external parameter much like it is in the more typical Langevin equation approach. In the present case, the only control of the relative strength of fluctuations is through the system size. This idea will be made more precise in the next section.

III. PARAMETERS FOR STOCHASTIC RESONANCE

In accord with other investigations of stochastic resonance, we look for regimes in which the deterministic potential shows bistability. Our situation, however, is not one which affords ready extraction of a deterministic component from the stochastic evolution. In the master equation, Eq. (2.2), fluctuations are inherent to the dynamics. One method of relating our model to previous studies is by performing a Kramers-Moyal expansion on Eq. (2.2). The result is a Fokker-Planck equation in the intensive variable $x=n/V$ which is equivalent to the Langevin equation

$$\frac{dx}{dt}=f(x,t)+\frac{1}{V}g(x,t)\xi(t)\ , \tag{3.1}$$

where the deterministic drift $f(x,t)$ is

$$f(x,t)=-V^2x^3+(\alpha+3)Vx^2-(\alpha+\beta+2)x+\frac{1}{V}\gamma(t)\ , \tag{3.2}$$

and the noise strength $g(x,t)$ is

$$g(x,t)=\sqrt{V^3x^3+(\alpha+3)V^2x^2+(\alpha+\beta+2)Vx+\gamma(t)}\ . \tag{3.3}$$

$\xi(t)$ is white noise defined by $\langle\xi(t)\rangle=0$, and $\langle\xi(t_1)\xi(t_2)\rangle=\delta(t_2-t_1)$.

[Obtaining Langevin equations from birth-death master equations is somewhat controversial. The principle approaches give the same asymptotic results in the large volume limit. For a discussion of this point, see [11]. We are not so much concerned with the details of the Langevin approximation because its purpose for us is simply to make a connection with previous work; the subsequent analysis is entirely on the original master equation, Eq. (2.2).]

We first note that in the absence of noise Eq. (3.1) can

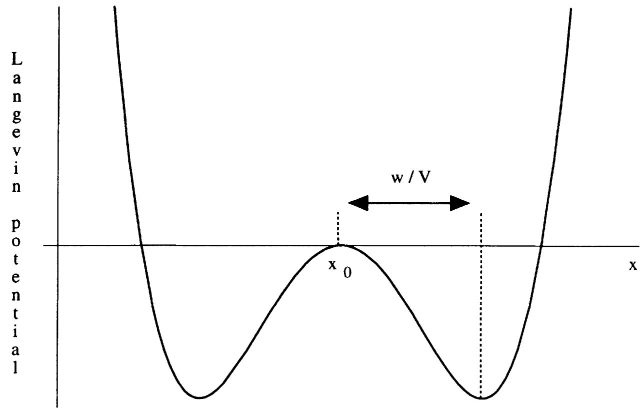

FIG. 1. The Langevin potential in its symmetric configuration. $x=n/V$ is the intensive variable.

be cast in the form

$$\frac{dx}{dt}=-V^2(x-x_0)^3+w^2(x-x_0)+\frac{1}{V}\epsilon\cos 2\pi f_0 t \tag{3.4}$$

by choosing

$$\alpha=3(Vx_0-1)\ , \tag{3.5a}$$

$$\beta=3(V^2x_0^2-Vx_0+1)-w^2-2\ , \tag{3.5b}$$

$$\gamma(t)=V^3x_0^3-w^2Vx_0+\epsilon\cos(2\pi f_0 t)\ . \tag{3.5c}$$

With this choice of parameters, the drift is described by a quartic, double-well potential which, in its symmetric configuration, is described by a distance w/V from each relative minimum to the central barrier at x_0 (Fig. 1). The harmonic component of γ causes the two minima to rise and fall asymmetrically. To ensure bistability, we require $\epsilon<\epsilon_{max}=2w^3/\sqrt{27}$.

The additional transformation $y=V(x-x_0)/w$, $s=w^2t$ casts Eq. (3.4) into the standard form

$$\frac{dy}{ds}=-y^3+y+\tilde{\epsilon}\cos 2\pi\tilde{f}_0 s\ , \tag{3.6}$$

where the scaled driving strength $\tilde{\epsilon}=\epsilon/w^3$, and the scaled driving frequency $\tilde{f}_0=f_0/w^2$. In this scaling and for the values of ϵ, f_0, and w used in the subsequent analysis, $\tilde{\epsilon}$ is on the order of 10^{-1}, $\tilde{f}_0$ is on the order of 10^{-2}, and the noise strength at the barrier is on the order of 10^{-1}.

Second, we note that the noise strength $g(x,t)$ of Eq. (3.3) is an increasing function of x. Low-concentration environments are less noisy than high-concentration environments. We see that as w increases, the minimum of the low-concentration well moves to yet lower concentrations, and the noise level in that well diminishes. Therefore trapping is possible in the low-concentration well if the well-width parameter w is sufficiently large. For any width of the double well, the high-concentration well will be relatively noisy, so the concentration readily jumps from this well. The width parameter w thus serves as our noise parameter, increasing width corresponding to decreasing noise.

For a stochastic resonance, we want the concentration to escape one well and return in one period, $T=1/f_0$, of the external driving force. This can be achieved by driving the system at a frequency on the order of the escape rate from a well in its symmetric configuration [12]. We calculate the escape time using the original master equation, Eq. (2.2). The time from the bottom of a well at the site n_0+w to the central barrier at the site n_0 in the time-independent case $\epsilon=0$ is [11]

$$\tau=\sum_{l=n_0}^{n_0+w}\phi_l\sum_{m=l}^{n_{\max}}\frac{1}{t_m^+\phi_m}\ , \tag{3.7}$$

where

$$\phi_n=\prod_{m=n_0+1}^{n}\frac{t_m^-}{t_m^+}\ , \tag{3.8}$$

with $t_m^{\pm}$ given by Eqs. (2.3a) and (2.3b) with $\epsilon=0$. We choose $n_{\max}=2n_0$. This is far enough from the stable states so that probability does not approach it. In this manner we chose $f_0=390$ based on a well width $w=200$.

IV. NUMERICAL SOLUTIONS OF THE MASTER EQUATION

Numerical solutions $P_n(t)$ of the master equation, Eq. (2.2), which is actually a semi-infinite set of coupled, ordinary differential equations labeled by the population number n, can be obtained by truncating the system. We integrated Eq. (2.2) by imposing a reflecting boundary at $n_{\max}=2n_0$. The long-time solution is periodic with period T. In Fig. 2, solutions $P_n(t)$ are illustrated in contour graphs for the case $n_0=400$, $f_0=390$, $\epsilon=0.8\epsilon_{\max}$, and three potential widths $w=100$, 200, and 300. For the small-width (large-noise) case, probability is distributed generously across the entire width of the double well with little trace of the periodic forcing. The population crosses from one side to the other essentially at will. At the other extreme, when the width is large and relative fluctuations are small, the probability is distributed almost exclusively around the low-population state. It drops to zero in a broad zone around the barrier. This is near the trapping regime. At intermediate width, the probability shifts periodically from one state to the other. It is decreased around the barrier except at the crossing times. This is the stochastic resonance regime.

Notice that the probability distribution is heavily weighted toward the smaller of the two stable population states even though the deterministic potential does not reflect this. We see that in this case the stochastic and deterministic potentials are quite different because, as discussed in Sec. III, the noise is not simply additive as it is in most previous studies of stochastic resonance (for an exception, see Ref. [13]). The difference between stochastic and deterministic potentials in the case of the undriven Schlögl model is pointed out in Ref. [14].

V. TIME SERIES AND POWER SPECTRA

The dynamics determined by the master equation, Eq. (2.2), can also be seen through realizations. The master equation describes a Markov process: each subsequent population size depends only on the current population size and transition probabilities. This permits a straightforward method of generating realizations [15]. One chooses an initial time and population and then picks two

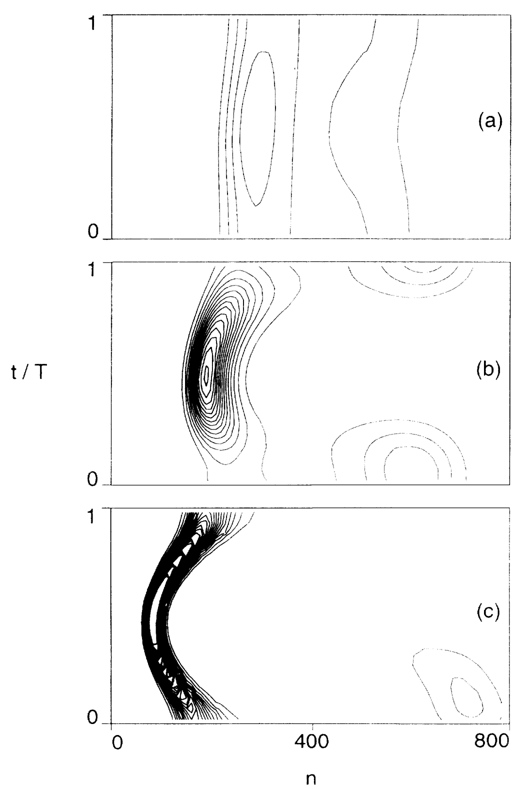

FIG. 2. Contour plots of the probability distribution $P_n(t)$ for the case $n_0=400$, $f_0=390$, and $\epsilon=0.8\epsilon_{\max}$. (a) $w=100$. (b) $w=200$. (c) $w=300$. The contour spacing is 0.001.

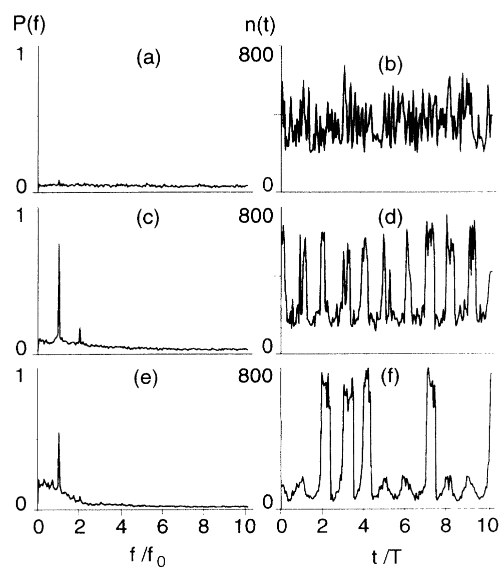

FIG. 3. Power spectra (left) and representative time series (right) for the case $n_0=400$, $f_0=390$, and $\epsilon=0.8\epsilon_{\max}$. (a) and (b) $w=100$; the SNR is 0.559. (c) and (d) $w=200$; the SNR is 6.37. (e) and (f) $w=300$; the SNR is 2.98.

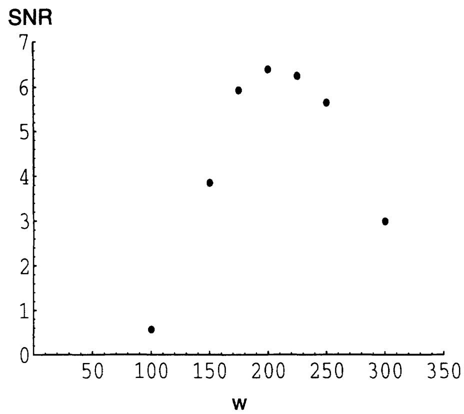

FIG. 4. Signal-to-noise ratio as a function of the width of the double well. Because the width plays the role of noise parameter, the peak is a trademark of stochastic resonance.

random numbers. The first, Poisson distributed, determines the wait time until the next transition. The second, distributed in proportion to the left and right transition probabilities, Eqs. (2.3), determines whether the population decreases or increases by one. The time and population are updated and the process is repeated as many times as desired. Time series of the realizations are easily obtained; power spectra follow by fast Fourier transform. The time series are windowed to reduce the edge effects, and 20 spectra are averaged to obtain the power spectra shown in Fig. 3. Signal-to-noise ratios (SNR's) are calculated by subtracting the ambient power in the neighborhood of the signal frequency from the total power in the bin centered on the signal frequency and then dividing by the ambient power. The frequency resolution of the spectra used in these calculations is $0.05f_0$, and the ambient power is the averaged power over the five bins on either side of the signal bin. Also shown are representative portions of the corresponding time series. For the small-width (large-noise) case, the power spectrum is dominated by background noise with little trace of the periodic signal. The SNR is $(0.0866-0.0555)/0.0555=0.559$. At intermediate width, the power spectrum shows a sharp peak at the signal frequency. The SNR is $(0.755-0.102)/0.102=6.37$. This is the stochastic resonance regime. When the width is large and relative fluctuations are small, the peak at the signal frequency has diminished substantially. The SNR is $(0.544-0.137)/0.137=2.98$. This is near the trapping regime. Figure 4 shows a more detailed picture of the behavior of the SNR as the width of the double well varies. That the SNR exhibits a maximum with respect to noise is a trademark of stochastic resonance.

VI. CONCLUSIONS

In its first application to the ice ages, stochastic resonance offered a mechanism for anomalous behavior in what was, quite literally, a global system. In smaller systems, such as the autocatalytic reactions found in biochemistry, the internal dynamics alone could trigger a strong oscillatory response even when the driving fields are relatively weak. Indeed, periodic perturbation is quite common in biochemical systems, for example, by light, temperature, chemical, or electrical forcing, and such forcing can lead to product enhancement and selectivity (see, e.g., Ref. [16]). We are currently investigating whether the behavior demonstrated in this Brief Report persists in higher-dimensional models more representative of those situations.

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[1] R. Benzi, A. Sutera, and A. Vulpiani, J. Phys. A **14**, L453 (1981).
[2] C. Nicolis and G. Nicolis, Tellus **33**, 225 (1981).
[3] S. Fauve and F. Heslot, Phys. Lett. **97A**, 5 (1983).
[4] B. McNamara, K. Wiesenfeld, and R. Roy, Phys. Rev. Lett. **60**, 2626 (1988).
[5] L. Gammaitoni, M. Martinelli, L. Pardi, and S. Santucci, Phys. Rev. Lett. **67**, 1799 (1991).
[6] André Longtin, Adi Bulsara, and Frank Moss, Phys. Rev. Lett. **67**, 656 (1991).
[7] Peter Jung, Ulrich Behn, Eleni Pantazelou, and Frank Moss, Phys. Rev. A **46**, R1709 (1992).
[8] P. De Kepper and J. Boissonade, in *Oscillations and Traveling Waves in Chemical Systems*, edited by J. Field and M. Burger (Wiley, New York, 1985), pp. 223–256.
[9] F. Schlögl, Z. Phys. **253**, 147 (1972).
[10] David S. Leonard, Phys. Rev. A **46**, 6742 (1992).
[11] C. W. Gardiner, *Handbook of Stochastic Methods for Physics, Chemistry and the Natural Sciences*, 2nd ed. (Springer-Verlag, Berlin, 1985).
[12] B. McNamara and K. Wiesenfeld, Phys. Rev. A **39**, 4854 (1989).
[13] M. I. Dykman, D. G. Luchinsky, P. E. V. McClintock, N. D. Stein, and N. G. Stocks, Phys. Rev. A **46**, R1713 (1992).
[14] G. Nicolis and R. Lefever, Phys. Lett. **62A**, 469 (1977).
[15] D. Gillespie, J. Comput. Phys. **22**, 403 (1976).
[16] Paul Rehmus and John Ross, in *Oscillations and Traveling Waves in Chemical Systems* (Ref. 8), pp. 287–332.