Noise-induced enhancement of chemical reactions in nonlinear flows

Zonghua Liu, Ying-Cheng Lai,[a] and Juan M. Lopez
Department of Mathematics and Center for Systems Science and Engineering Research, Arizona State University, Tempe, Arizona 85287

(Received 31 October 2001; accepted 26 February 2002; published 20 May 2002)

Motivated by the problem of ozone production in atmospheres of urban areas, we consider chemical reactions of the general type: $A+B\rightarrow 2C$, in idealized two-dimensional nonlinear flows that can generate Lagrangian chaos. Our aims differ from those in the existing work in that we address the role of transient chaos versus sustained chaos and, more importantly, we investigate the influence of noise. We find that noise can significantly enhance the chemical reaction in a resonancelike manner where the product of the reaction becomes maximum at some optimal noise level. We also argue that chaos may not be a necessary condition for the observed resonances. A physical theory is formulated to understand the resonant behavior. © *2002 American Institute of Physics.*
[DOI: 10.1063/1.1476948]

The interplay between noise and nonlinear dynamics has long been a topic of tremendous interest in statistical physics. While noise can be detrimental in many situations, it can also be beneficial through, for example, the mechanisms of stochastic and coherence resonances. Recently, a new area of interdisciplinary science has emerged: active processes in nonlinear flows. Such processes can be chemical or biological, and are believed to be relevant to a large number of important problems in a variety of areas. Our work focuses on the role of noise in active nonlinear processes. In particular, we investigate how noise influences a general type of chemical reaction, supported on a chaotic flow. To be as realistic as possible, we take into consideration important physical effects such as particle inertia and finite size. Our finding is that noise can enhance the rate of a chemical reaction, in a manner similar to that of stochastic resonance. We provide numerical results and also a physical theory, suggesting that at a fundamental level, the resonant behavior is due to the interaction between noise and nonlinearity of the particle (Lagrangian) dynamics. It is hoped that this preliminary work will stimulate further research in the exciting area of stochasticity and active nonlinear dynamics.

I. INTRODUCTION

In this paper we investigate the role of noise in the dynamics of chemical reactions in bounded flows that can generate Lagrangian chaos. Our motivation comes from the desire to understand and quantify the dynamical processes governing the conversion of pollutants, such as those emitted from road traffic or industrial plants in major urban areas, to toxic agents that post a significant threat to public health. The conversion process is generally accomplished by a chain of chemical reactions supported on atmospheric flows that can be either regular, chaotic, or even turbulent. A detailed account of the problem, which includes an accurate modeling of the atmospheric flows under various boundary conditions and assessment of the physical chemistry associated with the reactions, is extraordinarily sophisticated and is beyond the scope of this study. To gain understanding, our approach is to investigate the dynamics of an *idealized* class of chemical reactions using an *idealized* model of nonlinear flow in a simplified manner. In particular, we will investigate chemical reactions of the form

$$A+B\rightarrow 2C, \tag{1}$$

where both A and B are reactants, C is the product, and the reactions are assumed isothermal and to occur on a prescribed nonlinear flow in two dimensions that can support Lagrangian chaos, specifically containing chaotic attractors or nonattracting chaotic saddles in the phase space. The main goal of this paper is to understand how the concentration of the product C is affected when the Lagrangian dynamics of the flow are regular or chaotic, *under the influence of noise*. Our principal result is that noise can significantly enhance the chemical reaction, in a resonancelike manner where the product of the reaction increases and then decreases as the noise amplitude is increased, and reaches a maximum at some optimal noise level. In fact, the resonancelike behavior can occur regardless of whether the asymptotic attractor is chaotic or regular. Thus, in a realistic situation where noise is present, to distinguish between chaotic and regular motions is not important for the particular problem of chemical reaction in flows.

The physical-chemistry background of our problem is as follows.[1] When fossil fuels are burned, a variety of pollutants are emitted into the Earth's troposphere, i.e., from ground level up to about 15 km. The pollutants emitted are of two classes, hydrocarbons (e.g., unburned fuel) and nitric oxides. Nitrogen oxides are formed during high-temperature combustion processes from the oxidation of nitrogen in the air or fuel. The principal source of nitrogen oxides is road traffic, and their concentrations are therefore greatest in urban areas

[a]Also at Departments of Electrical Engineering and Physics, Arizona State University, Tempe, Arizona 85287.

where traffic is heaviest. When these pollutants build up to sufficiently high levels, a chain reaction occurs from their interaction with sunlight, producing photochemical pollutants such as ozone. Ozone is a powerful oxidizing agent, and a toxic gas. Since ozone itself is photodissociated (split up by sunlight) to form free radicals, it promotes the oxidation chemistry, and so catalyses its own formation (i.e., it is an autocatalyst). Consequently, high levels of ozone are generally observed during hot, still, sunny summer-time weather in locations where the air mass has previously collected emissions of hydrocarbons and nitrogen oxides (e.g., urban areas with traffic). Because of the time required for chemical processing, ozone formation tends to be downwind of pollution centers. The resulting ozone pollution or summer-time smog may persist for several days and be transported over long distances.

Here, we do not attempt to model the complicated chemical reactions described above, but rather implement a very idealized model of the chemistry. The air pollution problem involves dozens of species and reactions, here we only consider three species and a single reaction. The correspondence between the chemicals in the model reaction (1) and the air pollution problem may be viewed as the following: *A*, *B*, and *C* represent nitrogen oxides, hydrocarbons, and ozone, respectively, and the reaction simulates the process of ozone production via the reaction between nitrogen oxides and hydrocarbons.

Chemical reactions, or active processes,[2] in chaotic hydrodynamic flows were first addressed in the pioneering works by Muzzio and Ottino[3] and by Metcalfe and Ottino.[4] The problem has since attracted an increasing amount of attention.[5–10] Recent studies[9,10] hint that active processes in chaotic flows may be highly relevant to the problem of ozone depletion associated with chlorine deactivation, which can be caused by hydrodynamic stirring and mixing.[11,12] The studies by Toroczkai *et al.*[9] on active processes in open chaotic hydrodynamic flows indicate that the underlying fractal structure of the chaotic invariant set may account for the observed filamental intensification of activity in environmental flows.[11,12] Active processes in chaotic flows are also conjectured to be relevant to the important problem of species coexistence in ecology.[13] In all these works, the reactants are assumed to be massless passive point particles. More recently, the effects of inertia and finite size on active particle dynamics in bounded hydrodynamic flows with time-periodic forcing have been investigated[14] for the coalescence type of reaction: $B+B\rightarrow B$. Because of the coalescent nature of the reaction, the number of particles decreases in time. A principal result from Ref. 14 is that the decay in the particle density $n(t)$ obeys the universal scaling law: $n(t)\sim t^{-1}$. Technically, our study differs from previous studies in that we focus on the influence of noise on a more general type of chemical reaction (1), and incorporate both particle inertia and finite size.

It should be noted that noise-induced resonance has been well known in nonlinear dynamics and statistical physics. There are two major phenomena: stochastic resonance[15–17] and coherence resonance.[18–21] Broadly speaking, stochastic resonance means that performances of the system, such as the response to periodic signals, can be enhanced by the noise and be made optimal at certain nonzero noise levels. This phenomenon is rather counterintuitive, but the mechanism lies in the complex interplay between nonlinearity and stochasticity.[15–17] Coherence resonance, on the other hand, means that the temporal regularity of signals from a nonlinear system can be enhanced by noise. The enhancement of chemical production by noise investigated in this paper is thus a stochastic resonant phenomenon. As we will describe later, the mechanism responsible for the enhancement is in fact a coherence resonance with respect to the dynamical behavior of particle trajectories. Our work thus represents an interesting example where a coherence resonance leads to stochastic resonances.

The rest of the paper is organized as follows. In Sec. II, we describe our model of deterministic flow. In Sec. III, we present numerical results demonstrating the role of noise and the resonant behavior. Section IV gives a physical theory for the observed resonance. A discussion is presented in Sec. V.

II. MODEL

The chemical reaction (1) gives a low-order simulation of ozone production via the reaction between nitrogen oxides and hydrocarbons. To gain insight, here we consider the simple situation where these active processes take place within a prescribed time-periodic flow. A common theoretical approach is to assume that the reactants are massless point particles advected by the flow, and as such the properties of the flow are unchanged by the particles.[9] More realistically, the reactants have both inertia and buoyancy. These physical effects can be summarized as the force exerted on the reactants by the undisturbed flow (the buoyancy force), the Stokes drag, the added mass effect, and other corrections.[22–24] A mathematical model incorporating all these effects will in general be quite sophisticated.

To make analysis and numerical computation feasible, we consider two-dimensional flows. Let $\mathbf{u}$ be the velocity of a fluid element, it can be described by a stream function $\psi(x,y,t)$ as $\mathbf{u}=\nabla\times\Psi$, where $\Psi=(0,0,\psi)$. The day/night cycle in the process of ozone production can be modeled as an external periodic temporal forcing. We choose the following stream function that has been utilized as a simple model to describe the distribution of plankton caused by the cellular motion induced by winds in lakes and oceans:[25]

$$\psi(x,y,t)=(1+k_0\ \sin(\omega_0 t))U_0 L\ \sin(x/L)\ \sin(y/L), \tag{2}$$

where U_0 is the velocity amplitude, L is the size of the vortex cell, k_0 and ω_0 are the amplitude and angular frequency of the temporal oscillation of the flow field (corresponding to the day/night forcing), respectively. Here the axes labeled by x and y are taken in the horizontal and vertical directions, respectively, with gravity pointing in the negative y direction. While the velocity of the fluid element derived from the stream function in (2) is indeed simple (time-periodic), particle trajectories can be extraordinarily complicated in the sense that chaos is commonly expected, which is the so-called Lagrangian chaos.[26] Let $\mathbf{V}$ be the velocity of the reacting particles (in units of U_0). Then, taking into account

both inertia and buoyancy, one can show that $\mathbf{V}$ obeys the following set of ordinary differential equations:[22–24,27]

$$\frac{d\mathbf{V}}{dt}=G(\mathbf{u}-\mathbf{V}+\mathbf{W})+R\left(\mathbf{u}+\frac{\mathbf{V}}{2}\right)\nabla\mathbf{u}+\frac{3R}{2}\frac{\partial\mathbf{u}}{\partial t}, \tag{3}$$

where $\mathbf{u}[\mathbf{Y}(t)]$ is the velocity field (in units of U_0) at the position $\mathbf{Y}(t)$ $[\mathbf{Y}\equiv(x,y)]$ of the reacting particles (in units of L). The dimensionless parameters G, R, and $\mathbf{W}$ can be expressed in terms of L, U_0, radius a of the reacting particle, its mass m_r, the fluid viscosity μ, the mass of the fluid m_f displaced by the reactant, and the gravitational acceleration g. In particular, parameter G represents the inertia effect and it is given by

$$G(m_r)=6\pi a\mu L/(U_0(m_r+m_f/2)),$$

where larger values imply smaller inertia effects, and

$$R(m_r)=m_f/(m_r+m_f/2)$$

is the buoyancy parameter. The regime $R>2/3$ describes bubbles and $R<2/3$ corresponds aerosols. The vector

$$\mathbf{W}(m_r)=(m_r-m_f)\mathbf{g}/(6\pi a\mu)$$

is the terminal velocity of the particle in still fluid.

Substituting the stream function (2) into the general flow model (3) yields the following set of five first-order differential equations governing the trajectories of each chemical species advected by the flow:

$$\begin{aligned}
&\frac{dx}{dt}=u,\quad \frac{dy}{dt}=v,\\
&\frac{du}{dt}=-Gu+(G(1+k_0\sin\phi)\\
&\qquad+\tfrac{3}{2}Rk_0\omega_0\cos\phi)\sin x\cos y+\tfrac{1}{2}R(1+k_0\sin\phi)\\
&\qquad\times(u\cos x\cos y-v\sin x\sin y)\\
&\qquad+R(1+k_0\sin\phi)^2\sin x\cos x,\\
&\frac{dv}{dt}=-Gv-(G(1+k_0\sin\phi)\\
&\qquad+\tfrac{3}{2}Rk_0\omega_0\cos\phi)\cos x\sin y+\tfrac{1}{2}R(1+k_0\sin\phi)\\
&\qquad\times(u\sin x\sin y-v\cos x\cos y)\\
&\qquad+R(1+k_0\sin\phi)^2\sin y\cos y+GW,\\
&\frac{d\phi}{dt}=\omega_0.
\end{aligned} \tag{4}$$

We remark that Eq. (4) is a highly simplified model for active particles advected by a nonlinear flow. In principle, for the air pollution problem it is necessary to study flows based on the solutions of the atmospheric fluid equations subject to boundary conditions that describe the geometry of the region of interest, and to incorporate the advection and diffusion of chemical reactants into the flow. To give a concrete example, we briefly describe the air pollution problem in Phoenix, USA. The atmospheric boundary layer in the Phoenix basin is typically well mixed to a height of several kilometers above the surface. The mixing results from destabilization of the lowest layers of the atmosphere by solar heating of the basin floor and the action of the resulting buoyant eddies. The mixing results in quantities such as the potential temperature being constant through the layer and the vertical shear of the horizontal wind being negligible. The layer is also capped by a stably stratified atmosphere. To capture the fundamental dynamics of the atmospheric boundary layer under the influence of localized heating, small scale terrain, and differential surface friction in the basin, the shallow-water equation with proper boundary conditions may be employed to yield the flow velocity field $\mathbf{u}$.[28–30] Chemical reactions can then be studied by using Eq. (3). Such a detailed study is nevertheless quite sophisticated but necessary for a future better understanding of active processes in realistic flows. In this paper we take the simple approach by assuming a particular flow field $\mathbf{u}$ for understanding the influence of noise on active processes. We stress that, in a more realistic model, while the flow field is typically described by solutions of nonlinear partial differential equations such as the Navier–Stokes equations or the shallow-water equation, the temporal evolution of physical particles advected by the flow is still described by ordinary differential equations such as Eq. (3).

The spatially periodic structure of the velocity field allows for the dynamics of the reactants to be considered as restricted to a basic cell $[0,2\pi]\times[0,2\pi]$ with periodic boundary conditions in both x and y. We find that chaos can occur commonly in the corresponding five-dimensional phase space. Typically, in such a case, particles tend to accumulate onto a fractal set.[27] To visualize the fractals, we make use of the idea of snapshot attractors.[31] Specifically, an ensemble of particles initialized randomly in a phase space region is evolved simultaneously in time and the locations of these particles at a later instant are recorded to yield a snapshot attractor of all particles. If the underlying dynamics is chaotic, the fractal structure can be seen even in the presence of random noise.[31] Figure 1 shows two examples of snapshot attractors obtained from the model Eq. (4), where the projections of the attractors in the (x,y) plane at $t=100$ are shown for the forcing amplitude $k_0=2.72$ and $k_0=3.10$ (other parameters used are $R=1.0$, $G=3.2$, $W=0.8$, and $\omega_0=\pi$). To obtain Figs. 1(a) and 1(b), 4×10^4 particles are uniformly distributed in the two-dimensional phase-space region: $-2\pi\leqslant[x,y]\leqslant2\pi$ with zero initial velocities. The particles are apparently concentrated on fractal sets.

The reason why it is necessary to use snapshot attractors to visualize the fractal structure of a chaotic attractor in the presence of noise can be seen, as follows. In a noiseless situation, a chaotic attractor typically exhibits a fractal structure. Under the influence of small random perturbations, the fractal pattern moves randomly in the phase space from time to time. As such, if one examines a long trajectory produced by the dynamics, one usually observes that the fractal structure is smeared out to a distance that scales with the strength of the perturbations. In order to see the fractal structure of the underlying chaotic attractor, a remedy is to ''freeze'' the

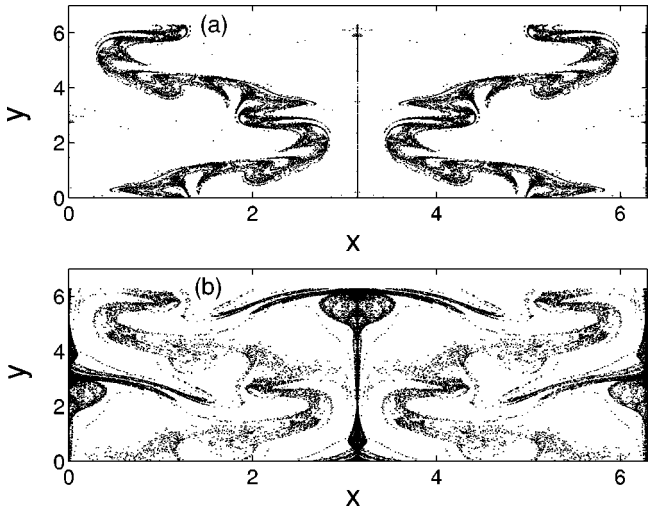

FIG. 1. Snapshot attractors at time $t=100$ for the forcing parameter (a) $k_0=2.72$ and (b) $k_0=3.10$, where in each case, 4×10^4 particles are initially uniformly distributed in the region: $-2\pi\leqslant[x,y]\leqslant2\pi$, and the trajectory of each particle is given by (4). Other parameters are: $R=1.0$, $G=3.2$, $W=0.8$, and $\omega_0=\pi$.

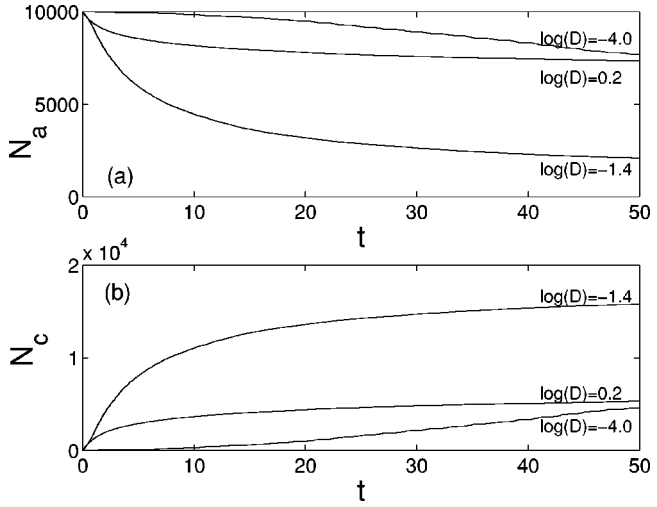

FIG. 2. Time histories of $N_A(t)$ and $N_C(t)$ for $R=1.0$, $G=3.2$, and $W=0.8$, with noise amplitudes $D=10^{-4}$ (relatively small noise), $D=10^{-1.4}$ (median noise), and $D=10^{0.2}$(relatively large noise). The reaction radius is $r=10^{-3}$.

time and examine the snapshot pattern formed by an ensemble of trajectories. Starting with a cloud of uniformly distributed initial conditions, after an initial transient time, one can indeed see the fractal structure of the snapshot attractors, provided that the influence of random noise on each particle is identical at any given instant of time. If the influences of noise on particles in the ensemble are slightly nonuniform, the fractal structure of a chaotic attractor can still be seen by using snapshots, but only for a transient period of time.[32]

Our goal is to study how the product of the chemical reaction, namely the concentration of C particles in (1) supported on a chaotic flow as described by (4), is affected by noise. To simulate the process of the chemical reaction, we fix a region in the two-dimensional physical space and launch a large number of particle species A and B into the region. The trajectories of A and B particles are determined by (4), but with different parameters, due to the difference in their masses. A reaction is considered to occur when an A particle and a B particle are sufficiently close to each other, say within a predetermined reaction radius r. As a result of this reaction, both the A and B particles are destroyed and two C particles are created. By energy conservation, both the energies of the A and B particles are transferred to that of two C particles. Once they have appeared, the C particles evolve according to (4) with parameters determined by the mass of the C particle. To model noise, we add to each of the equations in (4) (except for the last one that represents the periodic forcing), terms of the form $D\xi_i(t)$ $(i=1,\ldots,4)$, where D is the noise amplitude and $\xi_i(t)$'s are independent white noise terms. A standard first-order method is utilized for integrating the resulting stochastic differential equations (see the Appendix).

III. NUMERICAL RESULTS

To gain insight, we first consider the simple case where the masses of A and B are equal, i.e., the parameters R, G, and W for both particles are the same. We launch 10^4 A particles and the same number of B particles into the spatial region $-2\pi\leqslant(x,y)\leqslant2\pi$. Figure 2 shows, for $R=1.0$, $G=3.2$, $W=0.8$ at three difference noise levels, the time traces of $N_A(t)$ and $N_C(t)$, where the reaction radius is chosen to be $r=10^{-3}$; $N_A(t)$ and $N_C(t)$ are the numbers of A and C particles, respectively. For both relatively small and large noise levels ($D=10^{-4}$ and $D=10^{0.2}$), the production of C particles is slower than that in the case of median noise level ($D=10^{-1.4}$) in the initial phase of the reaction dynamics, say, for $t\lesssim10$. At larger times, the concentrations tend to saturate, indicating that most reactions occur for a short time following the initial mixing of active particles. This suggests the importance of transient dynamics in the sense that, due to the saturation, the resulting number of C particles at large times is mainly determined by their rate of initial production. That there are more C particles at the median noise level than those at small or large noise levels indicates a resonancelike behavior. This behavior can be seen more clearly in Fig. 3, where the A and C particles at different instants of time (filled circles: $t=10$; open circles: $t=20$; and stars: $t=50$) are plotted versus the noise amplitude.

We next consider the more realistic case where the masses of A and B particles are not equal: $m_A\neq m_B$. For convenience, we write $m_A=m_0+\Delta$ and $m_B=m_0-\Delta$, where m_0 is the average mass of an A and a B particle. Introducing the following *mass-imbalance* parameter:

$$\epsilon=\frac{\Delta}{m_0+m_f/2}, \tag{5}$$

the parameters R, G, and W for A and B particles in (4) become

$$\begin{aligned} R_{A,B}&=(1\pm\epsilon)R(m_0),\\ G_{A,B}&=(1\pm\epsilon)G(m_0),\\ W_{A,B}&=(1\pm3\epsilon)W(m_0). \end{aligned} \tag{6}$$

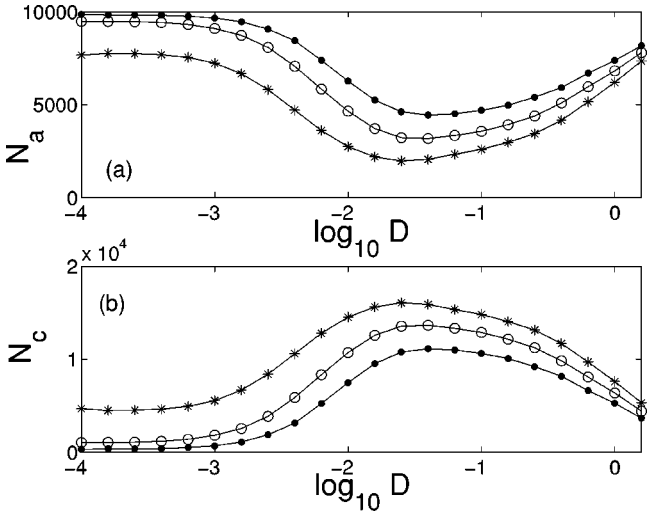

FIG. 3. $N_A(t)$ and $N_C(t)$ versus the noise amplitude D at $t=10$ (filled circles), $t=20$ (open circles), and $t=50$ (stars), for $R=1.0$, $G=3.2$, and $W=0.8$. A resonancelike behavior is seen in the sense that the resulting number of C particles reaches a maximum at a median noise level.

For illustrative purpose, we fix the forcing amplitude at $k_0=2.72$ and compute the largest Lyapunov exponent of the asymptotic attractor for one type of particle, say A, as a function of ϵ (the corresponding plot for the B particle can be obtained simply by making use of the symmetry: $\epsilon \to -\epsilon$). The result is shown in Fig. 4(a), where we see that there are parameter intervals of both chaotic attractors ($\lambda_1>0$) and periodic attractors ($\lambda_1=0$). The periodic attractors typically coexist with nonattracting chaotic saddles: there is thus transient chaos in the corresponding parameter intervals. For a randomly chosen initial condition, the resulting trajectory behaves chaotically for a transient amount of time before settling into the periodic attractor. Two examples of transient chaos are shown in Figs. 4(b) and 4(c), for $\epsilon=-0.04$ and $\epsilon=0.04$, respectively.

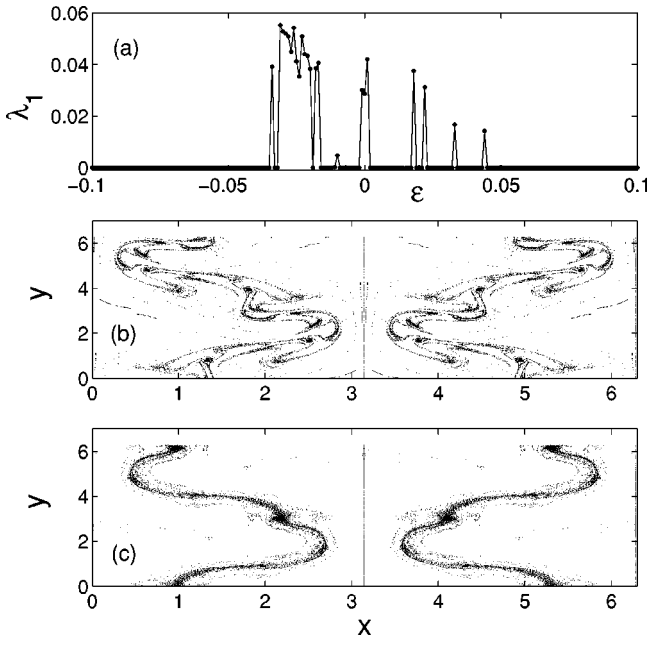

FIG. 4. (a) For fixed $k_0=2.72$, the largest Lyapunov exponent λ_1 versus the bifurcation parameter ϵ for particle A. The diagram for particle B is obtained by reversing the sign of ϵ. Examples of transient chaos for (b) $\epsilon=0.04$ and (c) $\epsilon=-0.04$, where snapshot attractors obtained at $t=100$ are shown.

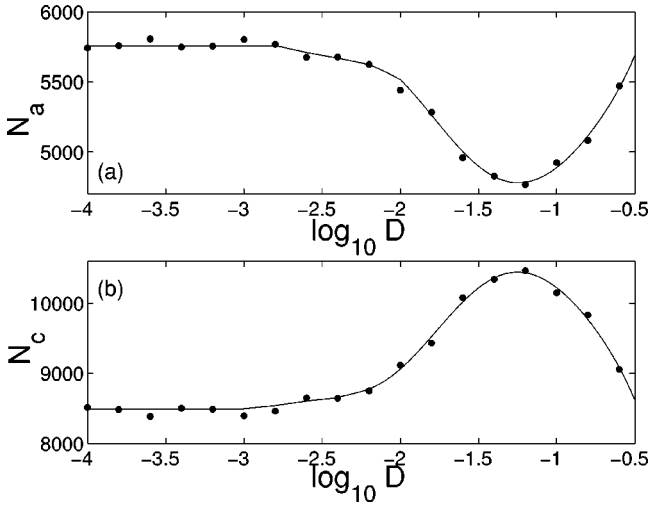

FIG. 5. $N_A(t)$ and $N_C(t)$ versus the noise amplitude D at $t=10$ and for $\epsilon=0.02$.

Since chemical reactions occur most intensely during the initial mixing of the reactants, we expect to observe a similar resonant behavior, regardless of whether the trajectories of the reactants are sustainedly chaotic or transiently chaotic, insofar as these reactants are injected into the reaction region in a time shorter than the average lifetime of the chaotic transients. This is verified by considering the following three combinations of the dynamics for A and B: (i) both on chaotic attractors, (ii) one on chaotic attractor and another being transiently chaotic, and (iii) both being transiently chaotic, and by computing the generation of C particles as a function of the noise amplitude. The results are shown in Figs. 5–7, where the numbers of A particles at $t=10$ versus $\log_{10} D$ are shown in panels (a), and those of C particles in panels (b). In Fig. 5, the mass-imbalance parameter is $\epsilon=0.02$, so both the A and B trajectories are sustainedly chaotic. In Fig. 6, ϵ

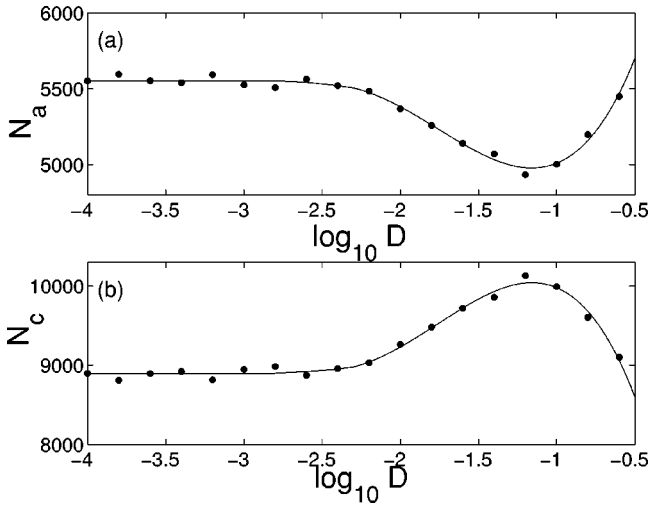

FIG. 6. $N_A(t)$ and $N_C(t)$ versus the noise amplitude D at $t=10$ and for $\epsilon=0.03$.

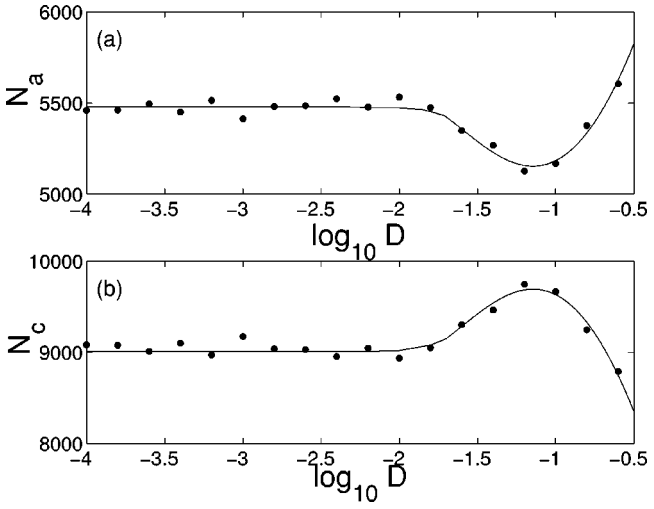

FIG. 7. $N_A(t)$ and $N_C(t)$ versus the noise amplitude D at $t=10$ and for $\epsilon=0.04$.

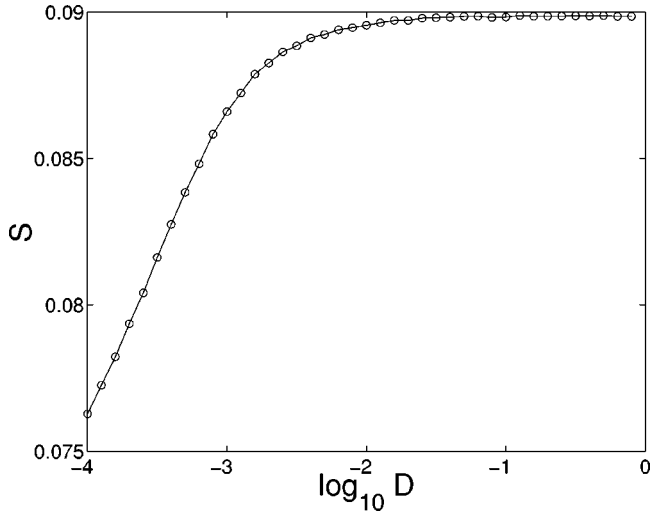

FIG. 8. Total reaction area S versus the noise amplitude D for $\epsilon=0.025$. The area remains approximately constant in the range of D where resonances are observed, indicating that area variation is not a contributing factor to the resonance.

$=0.03$ and the trajectories of one reactant is sustainedly chaotic and that of the other reactant is transiently chaotic. In Fig. 7, $\epsilon=0.04$ and the trajectories of both are transiently chaotic. Apparently, there is a consistent behavior of resonance, regardless of the nature of the Lagrangian chaotic dynamics, where noise of amplitude $D=D_m\sim 10^{-1.5}$ leads to a maximum production of the chemical C.

While Figs. 5–7 illustrate that both sustained and transient chaotic motions yield a similar resonant behavior, is chaos necessary for the resonance? Apparently, if there is no noise, chaos can facilitate the chemical reaction because the intrinsic ergodicity of chaos can help the reactants to meet in the phase space. If noise is small, this may still be the case. However, for large noise, trajectories of the reactants, even if they are periodic, will be fattened. Thus, if a resonant behavior is observed for large noise, chaos may not necessarily be a contributing factor. To gain insight, we compute the effective reaction area in the physical space for chaotic motion, which is determined by the regions that active particles can visit. Since in phase space, particle trajectories are concentrated near the chaotic invariant set, the geometric structure of the set, which is typically fractal, determines the reaction area. Under the influence of noise, one would expect an augmented reaction area because the fractal structure is typically fattened by noise. To see whether the change in the area contributes to the resonant behavior observed in Figs. 5–7, we initiate 9×10^4 particles in one cell and calculate the total reaction area at a later time, say $t=50$. The result is shown in Fig. 8, where we see that although the area increases at small noise levels, in the range of noise amplitude where resonances occur, the area remains essentially constant, indicating that the change in the area with noise is not a contributing factor to the resonant behavior. This result implies that for our particular model, chaos is not a necessary condition for the observed resonances. As we will argue later using a one-dimensional double-well potential model, resonance can occur simply as a direct consequence of the coherent switching of particles between the two wells.

IV. A PHYSICAL THEORY OF RESONANCE

The production of C particles through the chemical reaction in (1) is determined by the probability that A and B particles can get sufficiently close together. Intuitively, this probability is determined by two factors, (i) the effective reaction area in the physical space (the probability is inversely proportional to area), and (ii) the properties of the underlying chaotic flow, e.g., temporally more regular flows lead to larger probabilities. Figure 8 demonstrates, however, that the change in the reaction area due to noise is not a contributing factor to the resonant behavior. The numerically observed resonances are therefore mainly determined by the dynamical properties of the underlying invariant set.

Among the various dynamical characteristics of an invariant set, temporal regularity is the most relevant one that can influence the rate of the chemical reaction. To see this, we plot in Fig. 9 time traces $x(t)$ of the particle trajectories

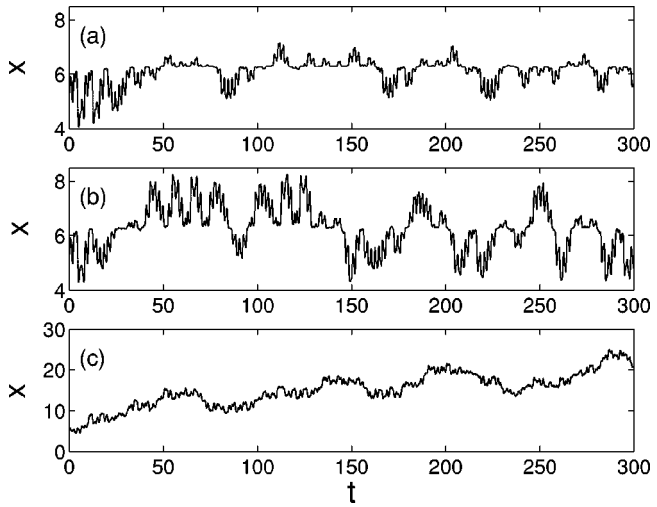

FIG. 9. Time traces $x(t)$ of the particle trajectories for (a) $D=10^{-2}$, (b) $D=10^{-1.5}$, and (c) $D=10^{-0.5}$.

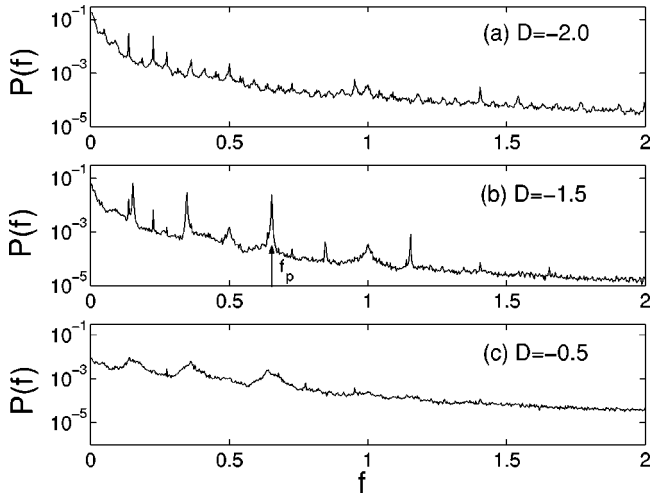

FIG. 10. Power spectra of the particle trajectories $x(t)$ for (a) $D=10^{-2}$, (b) $D=10^{-1.5}$, and (c) $D=10^{-0.5}$.

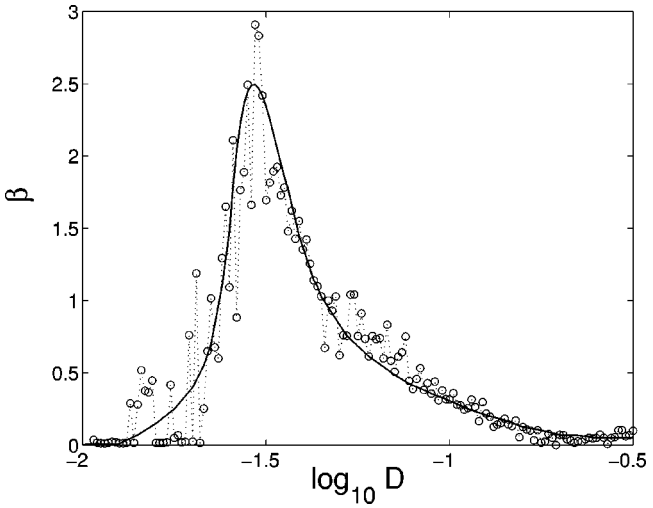

FIG. 11. The measure of temporal regularity β_S versus D. The resonant behavior in β_S is consistent with those seen in Figs. 5–7.

at three different noise levels about D_m: $D=10^{-2}$, $10^{-1.5}$, and $10^{-0.5}$, respectively, where for Figs. 9(a) and 9(b), the range of x values extends two adjacent 2π cells about $x=2\pi$. For $D=10^{-2}\lesssim D_m$, the particles spend most of the time in the lower cell ($0\leqslant x\leqslant 2\pi$), with occasional bursts into the upper cell ($2\pi\leqslant x\leqslant 4\pi$). For $D=10^{-1.5}\approx D_m$, the trajectory switches intermittently between the two cells; the switching behavior is apparently induced by noise. For $D=10^{-0.5}\gtrsim D_m$, the particle motion becomes diffusive in the sense that its trajectory crosses many cells. Heuristically, the occurrence of resonance can be reconciled as follows. Motion primarily restricted to one cell, as occurred in Fig. 9(a), is temporally highly irregular due to the combination of chaotic advection and noise. The probability for reaction to occur is relatively low. Frequent switching of the trajectory between adjacent cells, as in Fig. 9(b), can result in a ''coherence'' in the particle motion. More regular switchings result in more coherent motion of the chemicals advected by the flow, which can potentially lead to a higher probability of reaction. Finally, if the particle motion becomes diffusive, as in Fig. 9(c), the degree of coherence of the motion is reduced, resulting in a lower probability of reaction. The time scale most relevant for the chemical reaction is thus the *noise-induced switching time* between adjacent cells. If the above picture is correct, we expect to observe a relatively high degree of temporal regularity of the particle motion near D_m.

To characterize the temporal regularity of the particle motion, we compute the Fourier spectra of $x(t)$ for different noise levels. Figure 10 shows the spectra for $D=10^{-2}$, $10^{-1.5}$, and $10^{-0.5}$, respectively. Because of chaos and noise, the spectra are broad banded, but due to periodic forcing at frequency $f_0=\omega_0/2\pi=0.5$ and nonlinearity, there are spectral peaks at frequencies that are rationally related to f_0. The peak at $f_p\approx 0.65$, however, appears to be due to the noise-induced switching behavior of the particle trajectory. We thus focus on this spectral peak. The narrower and higher the peak is above the noisy background, the more regular the switching behavior. The temporal regularity can be conveniently characterized by the following measure:[19,20]

$$\beta_S = H f_p/\Delta f, \tag{7}$$

where H is the height of the spectral peak beyond the broadband background and $\Delta\omega$ is its half-width. Figure 11 shows, for the chaotic flow of (4) at the parameter setting of Figs. 5–7, the measure β_S versus the noise amplitude D, which exhibits a resonant behavior in the sense that β_S reaches maximum at $D\approx 10^{-1.5}$. The switching behavior is temporally most regular near D_m, which is consistent with the resonances observed in Figs. 5–7.

To understand the resonant behavior in β_S, we consider a heuristic model. From the point of view of mechanics, the noise-induced switching behavior of the particle motion is conceptually equivalent to motion in a double-well potential. Consider then the motion of a particle of unit mass in a one-dimensional, symmetric, double-well potential $V(x)$ under heavy damping. Suppose the motion is confined to one well without noise. The presence of noise can induce hopping of the particle from one well to another. For relatively small noise, the hopping events are rare, so the temporal regularity of the motion is determined by that of the noisy motion in an individual well. For median noise, hopping occurs more frequently and possibly becomes more regular. For large noise, the hopping becomes even more frequent and it is mainly determined by the noise. The motion is thus more irregular as compared with that at the medium noise. The key point here is that, with respect to hopping, noise can actually result in temporally more regular motions. As can be seen later, the simple mechanical model leads to a qualitatively similar resonant behavior to that observed in our five-dimensional model Eq. (4), suggesting that the common feature in both models, stochastic hopping, is the main contributing factor to the observed resonances.

We are thus led to consider the following equation of motion for a heavily damped mechanical particle:

$$\frac{dx}{dt} = -\frac{dV(x)}{dx} + D\xi(t), \tag{8}$$

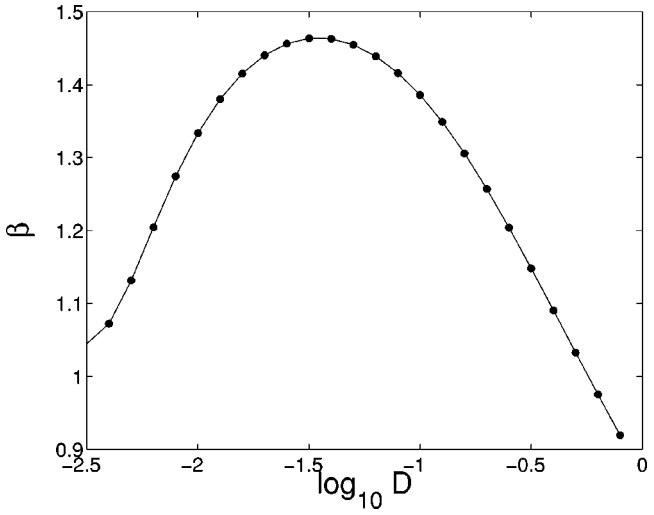

FIG. 12. Theoretically predicted measure of resonance β_T versus the noise amplitude D. The resonant behavior is consistent with those seen in the numerical experiments.

where $D\xi(t)$ models the noise and $\xi(t)$ is a white noise term, and the potential function is assumed to be the following double-well type:

$$V(x) = -\frac{a}{2}x^2 + \frac{b}{4}x^4, \tag{9}$$

where a and b are constants. To quantify how the temporal regularity of $x(t)$ is modulated by noise, we use the following measure introduced in Ref. 20 for convenience, which is equivalent to β_S:[33]

$$\beta_T = \frac{\langle T \rangle}{\sqrt{\mathrm{Var}(T)}}, \tag{10}$$

where T is the time interval between two consecutive switchings, and $\langle T \rangle$ and $\mathrm{Var}(T)$ are the mean and variance of $T(t)$, respectively. To obtain $\langle T \rangle$ and $\mathrm{Var}(T)$, we consider the Fokker–Planck equation associated with (8):

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}\left(-\frac{dV(x)}{dx}P\right) + \frac{D^2}{2}\frac{\partial^2 P}{\partial x^2}, \tag{11}$$

where $P(x,t)$ is the time-dependent probability distribution function of the random variable $x(t)$. Noting that the switching time T is in fact the first-passage time of the stochastic process $x(t)$, we solve (11) for quantities that are required for characterizing the time regularity of $x(t)$ under the conditions that there is an absorbing boundary at $x = x_a$ and a reflecting one at $x = x_b$. We obtain,[34] for the first and second moments of T, the following:

$$\begin{aligned} \langle T(x_0) \rangle &= \frac{2}{D^2}\int_{x_0}^{x_a}\int_{x_b}^{x} \exp\left(2\frac{V(x)-V(u)}{D^2}\right) du\ dx, \\ \langle T^2 \rangle &= \frac{4}{D^2}\int_{x_0}^{x_a}\int_{x_b}^{x} \langle T(u) \rangle \exp\left(2\frac{V(x)-V(u)}{D^2}\right) du\ dx, \end{aligned} \tag{12}$$

where x_0 is the initial value of $x(t)$. The quantity β_T can then be obtained from these moments. Figure 12 shows a typical behavior of β_T as a function of D that we obtain by numerically evaluating the integrals contained in the moments for the following parameters (arbitrary): $a = b = 10^{-4}$, $x_0 = -5$, $x_a = 0$, and $x_b = -20$. A resonant behavior can be seen clearly from Fig. 12, where β_T attains a maximum value at some optimal noise amplitude. This theoretical prediction is thus qualitatively consistent with the numerical plot of β_S in Fig. 11.

V. DISCUSSION

In this paper, we have developed an idealized computational model to investigate the dynamics of chemical reactions that produce air pollution. In particular, we utilize a prescribed time-periodic flow, whose vortical nature leads to chaotic particle trajectories (Lagrangian chaos). The time-periodic forcing is incorporated in consideration of the day/night diurnal cycle existing generally in the process generating air pollution. Going beyond existing works in this direction,[3,4,9,10,14] we pay particular attention to the nature of chaos, i.e., transient versus sustained, and we focus on the effect of random noise. Our results suggest that whether chaos is transient or sustained has little effect on the production of chemical reactions, but the influence of noise can be important. A resonant behavior exists in the sense that there is a small range of noise in which the production can be maximized. We give a heuristic theory, based on examining the temporal regularity of the Lagrangian motion of particles advected by the flow, to explain the numerically observed resonance behavior. We argue that whether the flow is chaotic has little influence on the resonant behavior. Perhaps then, in a realistic situation, it is environmental noise, rather than the nature of the underlying flow, which may play an important role in the generation of air pollution.

While our model is highly idealized as compared with realistic atmospheric flow, we incorporate important physical effects of particles advected by the flow such as inertia and finite-size. To our knowledge, such effects are considered in only one recent paper[14] that addresses the more tractable problem of advective coalescence in flows with chaotic trajectories. Investigating active processes in more realistic flow models is an interesting direction for future research.

ACKNOWLEDGMENTS

This work was sponsored by AFOSR under Grant No. F49620-98-1-0400 and by NSF under Grant No. PHY-9996454.

APPENDIX: INTEGRATION OF STOCHASTIC DIFFERENTIAL EQUATION

Our general model is a set of N stochastic differential equations of the following form:

$$\frac{dx_i}{dt} = F_i(\mathbf{x}) + G_i(\mathbf{x})\, D\epsilon(t), \tag{A1}$$

where $\mathbf{x}=\{x_1,x_2,\ldots,x_N\}$, $\epsilon(t)$ is a white noise term. It is convenient to use the Milshtein method,[35] which advances the solution forward in time according to the following recursive relations:

$$x_i(t+\delta t)=x_i(t)+\delta t\left(F_i(\mathbf{x})+\frac{D^2}{2}G_i(\mathbf{x})\frac{\partial G_i(\mathbf{x})}{\partial x_i}\right)+G_i(\mathbf{x})\,\eta_i(t)\sqrt{D^2\delta t}, \tag{A2}$$

where $\eta_i(t)$ is another white-noise term that is independent of $\epsilon(t)$. The inclusion of the term involving $\eta_i(t)$ is due to the fact that (A1) should be interpreted in the Stratonovich sense.[36] The Milshtein method is a first-order method, so the error at each integration step is on the order of $(\delta t)^2$. For D on the order of amplitudes of the dynamical variables $\mathbf{x}$, which represent all cases considered in this paper, the Milshtein method is efficient insofar as the integration step is small.[37]

[1] B. Sportisse and R. Djouad, J. Comput. Phys. **164**, 354 (2000); J. D. Fast, J. C. Doran, W. J. Shaw, R. L. Coulter, and T. J. Martin, J. Geophys. Res., [Atmos.] **105**, 22833 (2000); S. Bronnimann, W. Eugster, and H. Wanner, Atmos. Environ. **32**, 3789 (2001); E. J. Hutchinson, J. S. Mindell, and R. F. Warren, *ibid.* **35**, 1537 (2001).

[2] Here we take the word "active" to mean that the number of particles advected by the flow can change, due to chemical reactions, rather than the often used meaning that the property being advected alters the advecting flow.

[3] F. J. Muzzio and J. M. Ottino, Phys. Rev. A **40**, 7182 (1989); **42**, 5873 (1990).

[4] G. Metcalfe and J. M. Ottino, Phys. Rev. Lett. **72**, 2875 (1994); Chaos, Solitons, Fractals **6**, 425 (1995).

[5] I. R. Epstein, Nature (London) **374**, 321 (1995).

[6] S. Edouard, B. Legras, B. Lefevre, and R. Eymard, Nature (London) **384**, 444 (1996); S. Edouard, B. Legras, and V. Zeitlin, J. Geophys. Res. **101**, 16771 (1996).

[7] M. P. Chipperfield, E. R. Lutman, J. A. Kettleborough, J. A. Pyle, and A. E. Roche, J. Geophys. Res. **102**, 1467 (1997).

[8] M. G. Balluch and P. H. Haynes, J. Geophys. Res. **102**, 23487 (1997).

[9] Z. Toroczkai, G. Károlyi, A. Péntek, T. Tél, and C. Grebogi, Phys. Rev. Lett. **80**, 500 (1998); G. Károlyi, A. Péntek, Z. Toroczkai, T. Tél, and C. Grebogi, Phys. Rev. E **59**, 5468 (1999).

[10] Z. Neufeld, C. López, and P. H. Haynes, Phys. Rev. Lett. **82**, 2606 (1999); Z. Neufeld, C. López, E. Hernández-García, and T. Tél, Phys. Rev. E **61**, 3857 (2000).

[11] D. G. H. Tan, P. H. Haynes, A. R. MacKenzie, and J. A. Pyle, J. Geophys. Res. **103**, 1585 (1998).

[12] A. Mariotti, C. R. Mechoso, B. Legras, and V. Daniel, J. Atmos. Sci. **57**, 402 (2000).

[13] G. Károlyi, A. Péntek, I. Scheuring, T. Tél, and Z. Toroczkai, Proc. Natl. Acad. Sci. U.S.A. **97**, 13661 (2000); I. Scheuring, G. Károlyi, A. Péntek, T. Tél, and Z. Toroczkai, Freshwater Biol. **45**, 123 (2000).

[14] T. Nishikawa, Z. Toroczkai, and C. Grebogi, Phys. Rev. Lett. **87**, 038301 (2001).

[15] Stochastic resonance was first reported in R. Benzi, A. Sutera, and A. Vulpiani, J. Phys. A **14**, L453 (1981); R. Benzi, G. Parisi, A. Sutera, and A. Vulpiani, SIAM J. Appl. Math. **43**, 565 (1983).

[16] Stochastic resonance is such an extensive field that even a partial list of the literature is prohibitive here. For review of stochastic resonance, see, for example, P. Jung, Phys. Rep. **234**, 175 (1993); F. Moss, D. Pierson, and D. O'Gorman, Int. J. Bifurcation Chaos Appl. Sci. Eng. **4**, 1383 (1994); K. Wiesenfeld and F. Moss, Nature (London) **373**, 33 (1995); L. Gammaitoni, P. Hänggi, P. Jung, and F. Marchesoni, Rev. Mod. Phys. **70**, 223 (1998); references therein.

[17] Other representative papers include B. McNamara and K. Wiesenfeld, Phys. Rev. A **39**, 4854 (1989); A. Longtin, A. Bulsara, and F. Moss, Phys. Rev. Lett. **67**, 656 (1991); P. Jung, U. Behn, E. Pantazelou, and F. Moss, Phys. Rev. A **46**, R1709 (1992); J. K. Douglass, L. Wilkens, E. Pantazelou, and F. Moss, Nature (London) **365**, 337 (1993); K. Wiesenfeld and F. Moss, *ibid.* **373**, 33 (1995); J. J. Collins, C. C. Chow, and T. T. Imhoff, *ibid.* **376**, 236 (1995); J. J. Collins, C. C. Chow, and T. T. Imhoff, Phys. Rev. E **52**, R3321 (1995); M. E. Inchiosa and A. R. Bulsara, *ibid.* **52**, 327 (1995); C. Heneghan, C. C. Chow, J. J. Collins, T. T. Imhoff, S. B. Lowen, and M. C. Teich, *ibid.* **54**, R2228 (1996); M. E. Inchiosa and A. R. Bulsara, *ibid.* **53**, R2021 (1996); A. R. Bulsara and A. Zador, *ibid.* **54**, R2185 (1996); M. Misono, T. Kohmoto, Y. Fukuda, and M. Kunitomo, *ibid.* **58**, 5602 (1996); P. C. Gailey, A. Neiman, J. J. Collins, and F. Moss, *ibid.* **79**, 4701 (1997); F. Chapeau-Blondeau and X. Godivier, *ibid.* **55**, 1478 (1997); A. Neiman, L. Schimansky-Geier, and F. Moss, *ibid.* **56**, R9 (1997); M. E. Inchiosa, A. R. Bulsara, A. D. Hibbs, and B. R. Whitecotton, Phys. Rev. Lett. **80**, 1381 (1998); D. Nozaki, J. J. Collins, and Y. Yamamoto, Phys. Rev. E **60**, 4637 (1999); D. F. Russell, L. A. Wilkens and F. Moss, Nature (London) **402**, 291 (1999); I. Goychuk and P. Hänggi, Phys. Rev. E **61**, 4272 (2000); P. Hänggi, M. E. Inchiosa, D. Fogliatti, and A. R. Bulsara, *ibid.* **62**, 6155 (2000); P. E. Greenwood, L. M. Ward, D. F. Russell, A. Neiman, and F. Moss, Phys. Rev. Lett. **84**, 4773 (2000); M. E. Inchiosa, J. W. C. Robinson, and A. R. Bulsara, *ibid.* **85**, 3369 (2000); N. G. Stocks, *ibid.* **84**, 2310 (2000); I. Goychuk, Phys. Rev. E **64**, 021909 (2001); N. G. Stocks and R. Mannella, *ibid.* **64**, 030902 (2001); N. G. Stocks, *ibid.* **63**, 041114 (2001); N. G. Stocks, Phys. Rev. A **279**, 308 (2001).

[18] Sigeti and Horsthemke were the first to observe that noise can be utilized to improve the temporal regularity of physical signals, a phenomenon which they called *noise-induced frequency*. See, D. Sigeti and W. Horsthemke, J. Stat. Phys. **54**, 1217 (1989).

[19] G. Hu, T. Ditzinger, C. Z. Ning, and H. Haken, Phys. Rev. Lett. **71**, 807 (1993).

[20] A. S. Pikovsky and J. Kurths, Phys. Rev. Lett. **78**, 775 (1997).

[21] Representative papers on coherence resonance include A. Neiman, P. I. Saparin, and L. Stone, Phys. Rev. E **56**, 270 (1997); T. Ohira and Y. Sato, Phys. Rev. Lett. **82**, 2811 (1999); A. Neiman, L. Schimansky-Geier, A. Cornell-Bell, and E. Moss, *ibid.* **83**, 4896 (1999); J. R. Pradines, G. V. Osipov, and J. J. Collins, Phys. Rev. E **60**, 6407 (1999); D. E. Postnov, S. K. Han, T. G. Yim, and O. V. Sosnovtseva, *ibid.* **59**, R3791 (1999); S. K. Han, T. G. Yim, D. E. Postnov, and O. V. Sosnovtseva, Phys. Rev. Lett. **83**, 1771 (1999); B. Lindner and L. Schimansky-Geier, Phys. Rev. E **60**, 7270 (1999); **61**, 6103 (2000); B. Hu and C. Zhou, *ibid.* **61**, R1001 (2000); G. Giacomelli, M. Giudici, S. Balle, and J. R. Tredicce, Phys. Rev. Lett. **84**, 3298 (2000); Z. Liu and Y.-C. Lai, *ibid.* **86**, 4737 (2001); Y.-C. Lai and Z. Liu, Phys. Rev. E **64**, 066202 (2001).

[22] M. R. Maxey and J. J. Riley, Phys. Fluids **26**, 883 (1983).

[23] E. E. Michaelides, J. Fluids Eng. **119**, 233 (1997).

[24] A. Babiano, J. H. E. Cartwright, O. Piro, and A. Provenzale, Phys. Rev. Lett. **84**, 5764 (2000).

[25] I. Langmuir, Science **87**, 119 (1938).

[26] J. M. Ottino, *The Kinematics of Mixing: Stretching, Chaos, and Transport* (Cambridge University Press, New York, 1989).

[27] L. Yu, C. Grebogi, and E. Ott, in *Nonlinear Structure in Physical Systems* (Springer-Verlag, New York, 1990), pp. 223–231.

[28] A. E. Gill, *Atmosphere-Ocean Dynamics* (Academic, New York, 1982).

[29] M. DeMaria and J. D. Pickle, J. Atmos. Sci. **45**, 1542 (1988).

[30] J. A. Zehnder and M. J. Reeder, Meteorol. Atmos. Phys. **64**, 1 (1997).

[31] F. J. Romeiras, C. Grebogi, and E. Ott, Phys. Rev. A **41**, 784 (1990).

[32] Y.-C. Lai, Phys. Rev. E **60**, 1558 (1999).

[33] The quantity β_T is in fact equivalent to β_S, which can be seen as follows. A physical process can be described either in the time domain: $f(t)$, or in the frequency domain by its Fourier transform $F(\omega)$. When $f(t)$ is approximately periodic, its Fourier spectrum exhibits a peak at $\omega_p=1/\langle T\rangle$ with width $\Delta\omega$. Since $T\sim 1/\omega$, we have $\langle T\rangle+\Delta T\sim 1/(\omega_p+\Delta\omega)\approx 1/\omega_p-\Delta\omega/\omega_p^2$. Thus, $\Delta T\sim\Delta\omega/\omega_p^2$ and, hence, $\beta_T=\langle T\rangle/\Delta T\sim\omega_p/\Delta\omega\sim\beta_S$.

[34] C. W. Gardiner, *Handbook of Stochastic Methods* (Springer, Berlin 1983).

[35] P. E. Kloeden and E. Platen, *Numerical Solution of Stochastic Differential Equations* (Springer-Verlag, Berlin, 1992).

[36] R. L. Stratonovich, *Topics in the Theory of Random Noise* (Gordon and Breach, New York, 1967).

[37] C. Van den Broeck, J. M. R. Parrondo, R. Toral, and R. Kawai, Phys. Rev. E **55**, 4084 (1997).