The Effect of External Noise on Dynamic Behaviors of the Schlögl Model with the Second Order Transition for a Photochemical Reaction

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The method for the Schlögl model with the first order transition is extended to the Schlögl model with the second order transition for a photochemical reaction. We obtain the explicit results of the time-dependent average and the time correlation function at the unstable steady state of the model in the neighborhood of the Gaussian white noise and then discuss the effect of noise on the dynamic properties.

Introduction

In the preceding paper[1] we have investigated the effect of external noise on the dynamic behaviors in the Schlögl model with the first order transition for a photochemical reaction. Then, we have in detail discussed the effect of the external fluctuating light intensity on the stability of the steady states in the neighborhood of the Gaussian white noise by obtaining the explicit results of the time-dependent variance and the time correlation function with the aid of approximate results based on the stationary properties of the system. The main results are:

(1). The noise strength decreases the correlation time between the fluctuating macroscopic variables when the system is at the stable steady state. It has no effect on the stability of the system.

(2). The time correlation function directly shows that the external noise stabilizes the unstable steady state.

In this work, the method presented in the preceding paper is extended to the Schlögl model with the second order transition[2] for a photochemical reaction at the unstable steady state.

Theory

The Schlögl model with the second order transition may be written as

$$A+X \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2X+B,\quad X \xrightarrow{h\nu} C, \tag{1}$$

where k_1 and k_{-1} are the rate constants, A is the reactant and B and C denote the products. The rate equation for the concentration of the intermediate X is given by the following equation with the concentrations of A and B being held constants

$$\frac{dX}{dt} = -X^2+\gamma X-I(1-\exp-\alpha X);\ \gamma=\frac{k_1A}{k_{-1}B},$$

$$I=\frac{I_o}{k_{-1}B},\ t=k_{-1}B\tau. \tag{2}$$

In Eq. (2), X denotes the concentration of the intermediate; τ is the real time; I_0 is the incident light intensity and α is the absorption coefficient times the sample thickness. Let X_s and I_s be the values of X and I at a steady state. When $I_s>\gamma/\alpha$, there exists only one stable steady state, $X_s=0$. In the case of $I_s<\gamma/\alpha$, there are two steady states, that is, $X_s=0$ and $\gamma-\alpha I_s$ correspond to the unstable and stable steady states, respectively. Assuming that the light intensity satisfies the Ornstein-Uhlenbeck process and following the same procedure as in ref. 1, the fluctuating part $x=X-X_s=X$, which is the deviation from the unstable steady state due to the external fluctuating light intensity, satisfies the following Fokker-Planck equation in the neighborhood of the Gaussian white noise[1,3~4]

$$\frac{\partial}{\partial t}P(x,t)=\Big[-\frac{\partial}{\partial x}f(x)+\frac{\sigma^2}{2}\frac{\partial}{\partial x}g(x)\frac{\partial}{\partial x}h(x)\Big]P(x,t), \tag{3}$$

where σ is the strength of noise; $\varepsilon^2(\ll 1)$ is the inverse of the correlation time between the fluctuating intensities. The functions $f(x)$, $g(x)$, and $h(x)$ are defined as

$$f(x)=(\gamma-\alpha I_s)x-x^2,$$
$$g(x)=\exp(-\alpha x)-1,$$
$$h(x)=g(x)-\varepsilon^2[g(x)'f(x)-f(x)'g(x)]. \tag{4}$$

The stationary probability distribution at the unstable steady state is obtained, by including the ε^2 term, as

$$P_s(x)=P_{os}(x)\Big\{1-\varepsilon^2\Big[\frac{3}{2}(\gamma-\alpha I_s)+x+\frac{1}{\alpha^2\sigma^2}(\gamma-\alpha I_s-x)^2\Big]\Big\}; \tag{5}$$

$$P_{os}(x)=\frac{1}{\left(\frac{\alpha^2\sigma^2}{2}\right)^{\pm\beta}\Gamma(\pm\beta)}|x|^{\pm\beta-1}\exp-\frac{2|x|}{\alpha^2\sigma^2};\ \beta=\frac{2(\gamma-\alpha I_S)}{\alpha^2\sigma^2}, \tag{6}$$

where the perturbed term in Eq. (5) should be less than 1; $\Gamma(\pm\beta/2)$ is the gamma function and the upper and lower signs± represent the case of $x\geq 0$ and $x\leq 0$, respectively. The regions of $x\geq 0$ and $x\leq 0$ correspond to the cases of $I_s>\gamma/\alpha$ and $I_s<\gamma/\alpha$, respectively.[5] As already mentioned, $I_s>\gamma/\alpha$ is the necessary condition that the unstable steady state exists. Thus, from now on the case of $x>0$ is only discussed. The dependence of the stationary probability distribution on the light intensity and noise strength is shown in Figure 1a. The figure shows that the parameters affect the state of the

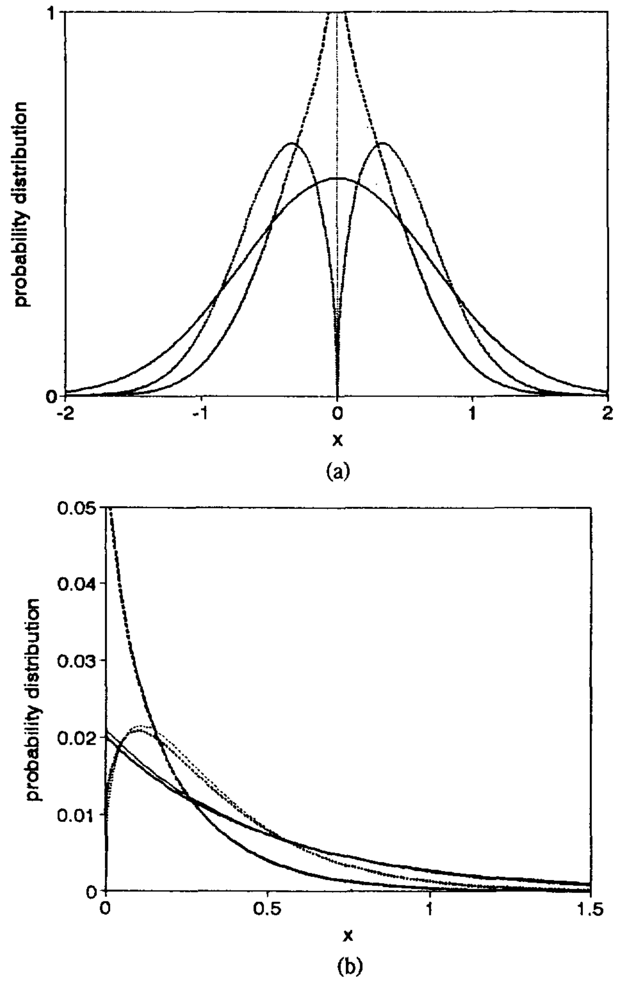

Figure 1. (a) The stationary probability distribution of Eq. (6). The heavy dotted, heavy solid and heavy dashed lines denote the distribution of $\beta=1.47$, 1 and 0.84, respectively. The values of parameters, when $\beta=1.47$, are $\gamma=2$, $\alpha=0.3$, $I_s=5.5$ and $\sigma=2.3$. In the case of $\beta=1$, $\gamma=2$, $\alpha=0.5$, $I_s=3$ and $\sigma=2$. When $\beta=0.84$, $\gamma=2$, $\alpha=0.3$, $I_S=6.0$ and $\sigma=2.3$. (b) The dependence of the probability distributions on the parameter, ε. The heavy and light lines denote $\varepsilon=0$ and 0.31, respectively. The lines of $\varepsilon=0.10$ correspond to those of $\varepsilon=0$. The values of other parameters are the same as in Figure 1a.

system profoundly. When $\beta>1$, the probability distribution is a distribution with the maximum at $x=-\gamma-\alpha I_s-\alpha^2\sigma^2/2$. The maximal peak shows that the deterministic stable steady state is shifted to $\gamma-\alpha I_s-\alpha^2\sigma^2/2$ due to the external noise. When $\beta=1$ and <1, the distribution is a gamma distribution and a delta-like distribution, respectively. As shown in Figure 1b, the distribution of $\varepsilon=0.1$ completely agrees with that of $\varepsilon=0$. When $\varepsilon=0.31$, it slightly deviates from that of $\varepsilon=0$. Thus, when $\varepsilon\ll1$, the term including ε^2 may be neglected. The average and nth order moments are

$$\langle x\rangle_s=\int_0^\infty x^2P_{os}(x)dx=\gamma-\alpha I_s, \tag{7a}$$

$$\langle x^n\rangle_s=\prod_{k=0}^{n-1}\langle x+k\frac{\alpha^2\sigma^2}{2}\rangle_s. \text{ if } n \text{ is an positive integer.} \tag{7b}$$

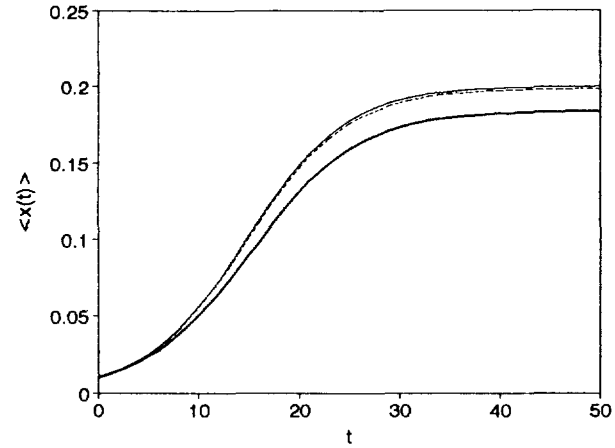

Figure 2. The dependence of $\langle x(t)\rangle$ on the parameter, ε. The solid, dashed and heavy solid lines represent $\varepsilon=0$, 0.10 and 0.31, respectively. The values of other parameters are $\gamma=2$, $\alpha=0.3$, $I_s=3$, $\langle x(0)\rangle=0.01$ and $\sigma=2.3$.

The time correlation function may be expressed as[1]

$$\frac{d}{dt}G(t)=(\gamma-\alpha I_s)G(t)-\langle x(t)^2x(0)\rangle. \tag{8}$$

Using the following relation

$$\langle x(t)^2x(0)\rangle=2\langle x(t)\rangle G(t), \tag{9}$$

the correlation function is written as

$$\frac{d}{dt}G(t)=[(\gamma-\alpha I_s)-2\langle x(t)\rangle]G(t). \tag{10}$$

With the aid of Eq. (3) $\langle x(t)\rangle$ satisfies

$$\frac{d}{dt}\langle x(t)\rangle=-(1+0.5\varepsilon^2\alpha^2\sigma^2)\langle x(t)^2\rangle+(\gamma-\alpha I_s+0.5\alpha^2\sigma^2)\langle x(t)\rangle. \tag{11}$$

Using the following relation based on Eq. (7b)

$$\langle x(t)^2\rangle=\langle x(t)\rangle[x(t)\rangle+\frac{\alpha^2\sigma^2}{2}], \tag{12}$$

we have

$$\frac{d}{dt}\langle x(t)\rangle=[-(1+0.5\varepsilon^2\alpha^2\sigma^2)\langle x(t)\rangle+(\gamma-\alpha I_s+0.25\varepsilon^2\alpha^2\sigma^2)]\langle x(t)\rangle. \tag{13}$$

The solution of Eq. (13) is

$$\langle x(t)\rangle=\langle x(0)\rangle(\gamma-\alpha I_S-0.25\varepsilon^2\alpha^2\sigma^2)\ \exp(\gamma-\alpha I_S-0.25\varepsilon^2\alpha^2\sigma^2)t \times\{\gamma-\alpha I_S-0.25\varepsilon^2\alpha^2\sigma^2-\langle x(0)\rangle(1+0.5\varepsilon^2\alpha^2\sigma^2) \times[1-\exp(\gamma-\alpha I_S-0.25\varepsilon^2\alpha^2\sigma^2)t]\}^{-1} \tag{14}$$

The dependence of $\langle x(t)\rangle$ on the parameter is shown in Fig. 2. The figure shows that for small ε, the results agree well with the case of the Gaussian white limit. For $t\rightarrow\infty$, the result approaches the value

$$\lim_{t\rightarrow\infty}\ \langle x(t)\rangle\approx\gamma-\alpha I_s-0.75\varepsilon^2\alpha^2\sigma^2. \tag{15}$$

When $\gamma-\alpha I_s\gg\varepsilon^2\alpha^2\sigma^2$, the result corresponds to that given

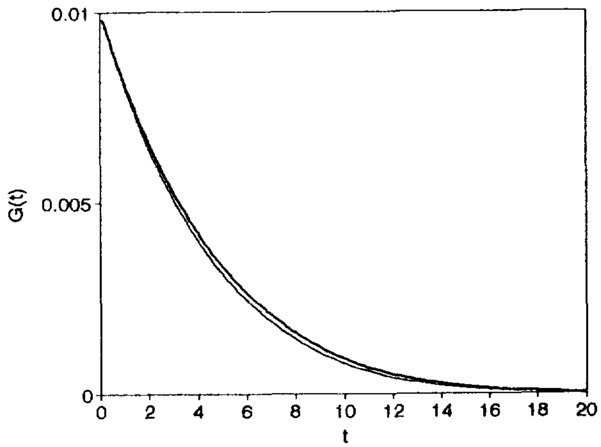

Figure 3. The time correlation function. The solid, dashed and heavy solid lines represent $\varepsilon=0$, 0.10 and 0.31, respectively. The solid and dashed curves completely coincide with each other. The values of the parameters are the same as in Figure 2.

in Eq. (7a). Let us consider the deterministic rate to show that the above result of Eq. (14) is quite reasonable.

$$\frac{d}{dt}x(t)=(\gamma-\alpha I_s)x(t)-x(t)^2. \tag{16}$$

The solution is

$$x(t)=\frac{x(0)(\gamma-\alpha I_s)\ \exp(\gamma-\alpha I_s)^t}{\gamma-\alpha I_s-x(0)[1-\exp(\gamma-\alpha I_s)t]}\ . \tag{17}$$

Neglecting the noise term, Eq. (14) reduces to Eq. (17), since the present stochastic process is based on the deterministic rate.

Substituting Eq. (14) into Eq. (10), we have

$$G(t)=G(0)\ F(t)\ \exp(\gamma-\alpha I_s)t, \tag{18}$$

where

$$\begin{aligned}F(t)=&(\gamma-\alpha I_s-0.25\varepsilon^2\alpha^2\sigma^2)^2\\ &\times\{\gamma-\alpha I_s-0.25\varepsilon^2\alpha^2\sigma^2-\langle x(0)\rangle(1+0.5\varepsilon^2\alpha^2\sigma^2)\\ &\times[1-\exp(\gamma-\alpha I_s-0.25\varepsilon^2\alpha^2\sigma^2)t]\}^{-2}\end{aligned} \tag{19}$$

An example of the time correlation function is given in Fig. 3. The example shows that for small ε the correlation functions correspond to that in the limit $\varepsilon\to 0$. After long time, the function becomes, neglecting the perturbed term,

$$G(t)\simeq G(0)\ \exp-(\gamma-\alpha I_s)t. \tag{20}$$

The results given in Eqs. (18) and (20) show that the nonlinear term stabilizes the unstable steady state.

Discussion

We have obtained the time correlation function in the Schlögl model with the second order transition at the unstable steady state. Let us remark some important points;

(1). The external noise strength severely affects the stationary probability distribution of the present model, as in the previous Schlögl model.[1]

(2). While the noise strength is quite important in the stabilization of the unstable steady state for the previous Schlögl model,[1] its effect on the present model can be neglected near the Gaussian white noise limit.

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