Some other examples are shown in Figures 6(b) and 6(c). As shown in the figures, the variation of the probability distributions by crossing the pitchfork bifurcation line is discontinuous.

Summary

We have compared the stationary probability distributions for the Schlögl model with the first order phase transition subjected to a multiplicative random force, which is singular at the deterministic unstable steady state by using the Ito and Statonovich methods for the stochastic process. Let us point out some important results.

(A) The multiplicative noise $|x|^{\nu}\ \xi(\tau)$ has an attracting (repelling) effect as $\nu>0$ ($\nu<0$), that is, it attracts (repels) the probability to (from) the unstable steady state. As $|\nu|$ increases, the attracting (repelling) force increases. The property competes with deterministic term in determining the stochastic properties of the system.

(B) When $\nu>0$, the stationary probability distribution becomes divergent at $x=0$. This result is clearly not realistic. Thus, a more realistic stochastic model should be proposed.

(C) The straight lines $\nu=0$ and $\nu=1$ give marginal situation, that is, the fluctuating intermediate undergoes the pitchfork bifurcation by crossing the lines and the variation of probability distributions becomes discontinuous, when the system undergoes the pitchfork phase transition.

(D) The diffusion coefficient with ν induces the saddle-node bifurcation in the case of $0<\nu<1$. Below the curve of the saddle-node bifurcation the coupling between the drift and noise terms plays the most important role. However, the multiplicative noise term becomes dominant above the curve. Thus, it is clear that the variation of probability distributions in the saddle-node transition is continuous.

(E) Even though the Ito and Stratonovich FPEs are based on the slight different definitions for the stochastic variable[8], some stochastic phenomena obtained from the equations are physically quite different, as shown in the previous section. Thus, it should be very careful to apply the Ito or Stratonovich FPE with multiplicative noise to an actual system.

In the following paper we shall discuss the stochastic phenomena for the Schlögl model with the second order transition subjected to the multiplicative noise singular at the unstable steady state.

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The Schlögl Model with the Second Order Transition Under the Influence of a Singular Multiplicative Random Force

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For the Schlögl model with the second order transition under the influence of the multiplicative noise singular at the unstable steady state, the detailed discussions are presented for various kinds of stochastic phenomena, such as the effects of parameters on stationary probability distribution, noise-induced phase transitions and escape rate.

Introduction

Recently, two of us[1] have discussed the stochastic phenomena for the Schlögl model with the first order transition driven by the multiplicative random force singular at the unstable steady state. The effects of the singularity on the stationary probability distribution have been analyzed in detail. Then, the transition rate has been discussed from one stable steady state to the other stable steady state through the unstable steady state. We[2] have also discussed and compared the effects of the parameters on the stationary probability distributions obtained by the Ito and Stratonovich methods.

The Schlögl model exhibiting the second order transition in chemical reaction is given by[3,4]

$$A+X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2X,\ B+X \xrightarrow{k_2} C \qquad (1)$$

where k_i's are the rate constants, A and B are the concentrations of reactants and C denotes that of product. The rate equation for X is given by the following equation while concentrations of other species being held constant

$$\frac{dX}{dt}=-k_{-1}X^2+(k_1A-k_2B)X \qquad (2)$$

Rewriting Eq. (2) in terms of the following scaled variables

$$\tau=k_{-1}t,\ \beta=(k_1A-k_2B)/k_{-1},$$

it reduces to

$$\frac{dX}{d\tau}=-X^2+\beta X \qquad (3)$$

When $\beta>0$, there are two steady states, that is, $X_0=\beta$ and $X_0=0$ corresponding to the stable and unstable states, respectively. In the case of $\beta<0$, there exists only one stable steady state with $X_0=0$.

In order to discuss stochastic phenomena for the model let us write a Langevin equation with a singular multiplicative noise (random force)

$$\frac{dX}{d\tau}=-X^2+\beta X+|X|^{\nu}\xi(\tau) \qquad (4)$$

with ν being an arbitrary number and the noise $\xi(\tau)$ being Gaussian and white

$$\langle\xi(\tau)\rangle=0,\ \langle\xi(\tau)\xi(\tau')\rangle=2D\ \delta(\tau-\tau'), \qquad (5)$$

where D is the diffusion coefficient and $\delta(\tau-\tau')$ is the Dirac delta function. The unstable steady state of the stochastic equation corresponds to that of the deterministic system. Eq. (4) can be rewritten in terms of $x=X-X_0=X$, which is the deviation from the unstable steady state due to the multiplicative noise, as

$$\frac{dx}{d\tau}=-x^2+\beta x+|x|^{\nu}\xi(\tau) \qquad (6)$$

According to the Ito and Stratonovich theories of the stochastic process,[5] the Langevin equation may be transformed to different Fokker-Planck equations (FPEs), that is,

$$\frac{\partial}{\partial\tau}P(x,\tau)=-\frac{\partial}{\partial x}[(-x^2+\beta x)P(x,\tau)]+D\frac{\partial^2}{\partial x^2}[|x|^{2\nu}P(x,\tau)] \qquad (7a)$$

$$\frac{\partial}{\partial\tau}P(x,\tau)=-\frac{\partial}{\partial x}[(-x^2+\beta x)P(x,\tau)] +D\frac{\partial^2}{\partial x}\left\{|x|\frac{\partial}{\partial x}[|x|^{\nu}P(x,\tau)]\right\} \qquad (7b)$$

The equations of (7a) and (7b) correspond to the Ito and Stratonovich results, respectively.

The purpose of the present paper is to discuss various kinds of stochastic phenomena, such as the effect of the exponent ν on the probability, noise-induced phase transitions, escape rate and etc., for the Schlögl model subjected to a mutiplicative random force, which is singular at the deterministic unstable steady state.

In the next section, the effects of the parameters on the stationary probability distribution obtained from the Ito method is discussed in detail. The escape rate for the system near the stable steady state is obtained in the following section. Finally, we point out some important results of the present work.

The Stationary Probability Distribution

We consider the Fokker-Planck equation obtained from Ito's theory first. Stratonovich's theory will be discussed later. The probability distribution of Eq. (7a) is given by the following expression:

$$P_I(x)=A\ \exp\{-V(x)/D\} \qquad (8)$$

where the subscript I means that the probability distribution is obtained from the Ito method, A is the normalization constant and

$$V(x)=\begin{cases}\frac{1}{3-2\nu}|x|^{3-2\nu}\mp\frac{\beta}{2(1-\nu)}|x|^{2-2\nu}+2\nu D\ \ln|x| & \text{for } \nu\neq1 \text{ and } 1.5,\\ |x|+(2D\mp\beta)\ \ln|x| & \text{for } \nu=1,\\ (1+3D)\ \ln|x|\pm\frac{\beta}{|x|} & \text{for } \nu=1.5.\end{cases} \qquad (9)$$

In Eq. (9) the upper and lower signs of $\mp$ and $\pm$ represent the cases of $x>0$ and $x<0$, respectively. When $\nu=1$, the probability diverges as x approaches to 0 negatively. In the case of $\beta>2D$ ($\beta<2D$) it vanishes (becomes infinite) as $x\to+0$. If $\nu=1.5$, the probability becomes divergent (zero), as $x\to-0$ ($+0$). The extrema of the probability in the cases of $\nu\neq1$ and $\nu\neq1.5$ may be obtained by solving the following algebraic equation

$$|x|^{3-2\nu}\mp\beta|x|^{2-2\nu}+2\nu D=0. \qquad (10)$$

Let us discuss two situations based on Eqs. (9) and (10).

(A) When $D\ll1$ and $\nu<0$, the maximal peak of $P_I(x)$ appears at

$$x_{1max}\simeq\beta(1-2\nu D\beta^{2\nu-3}) \qquad \text{for } x>0,$$

$$x_{2max}\simeq-\left(-\frac{2\nu D}{\beta}\right)^{1/(2-2\nu)}\times\left[1-\frac{1}{(3-2\nu)+2\beta(1-\nu)\left(-\frac{2\nu D}{\beta}\right)^{1/(2\nu-2)}}\right] \quad \text{for } x<0, \qquad (11)$$

For $x>0$, the multiplicative noise shifts the maximum peak of the probability farther away from the unstable state and a new maximum peak is created in the region of $x<0$ due to the coupling between the noise and the drift term. The probability for $\nu\ll0$ looks like a double Gaussian probability with peaks at x_{1max} and x_{2max}, that is,

$$P_I\simeq B\ \exp\left\{-\left[\frac{1}{2D}(x-x_{1max})^2\right]\right\}$$

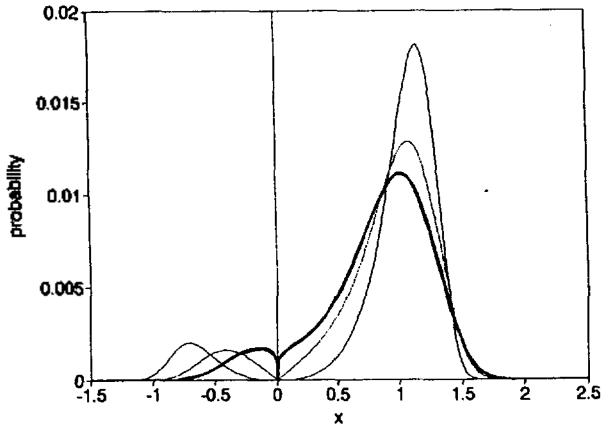

Figure 1. The stationary probability distribution for the case $\nu<0$ taking $D=0.1$ and $\beta=1$. The solid, dotted, and heavy solid curves denote $\nu=-1.5$, -0.5, and -0.1, respectively.

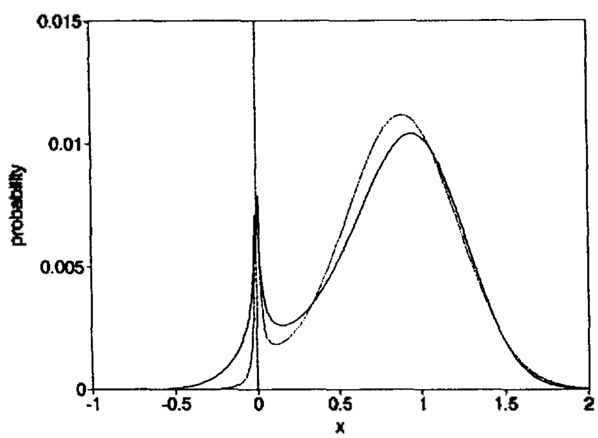

Figure 2. The stationary probability distribution for the case $\nu>0$ taking $D=0.1$ and $\beta=1$. The solid and dotted curves indicate $\nu=0.5$ and 0.25, respectively.

$$+B'\ \exp\left\{-\left[\frac{1}{2D}(x-x_{2max})^2\right]\right\}, \tag{12}$$

where B and B' are the normalization constants. As ν approaches to 0, the probability near the unstable steady state varies sharply near $x=0$ due to the multiplicative noise. As ν becomes negatively larger, the probability becomes farther away from the unstable steady state. Some examples are shown in Figure 1.

(B) If $D\ll 1$ and $0<\nu<1$, the maximal and minimal peaks appear at

$$x_{max}\simeq\beta(1-2\nu D\ \beta^{2\nu-3}) \qquad \text{for } x>0,$$

$$x_{min}\simeq\left(\frac{2\nu D}{\beta}\right)^{1/(2-2\nu)}\times\left[1-\frac{1}{(3-2\nu)-2\beta(1-\nu)\left(\frac{2\nu D}{\beta}\right)^{1/(2\nu-2)}}\right] \qquad \text{for } x>0, \tag{13}$$

For $x>0$ the multiplicative noise attracts the probability toward the unstable steady state and a new minimum peak is produced due to the coupling between the noise and drift terms. As x approaches to 0, the probability behaves as $1/x^{2\nu D}$

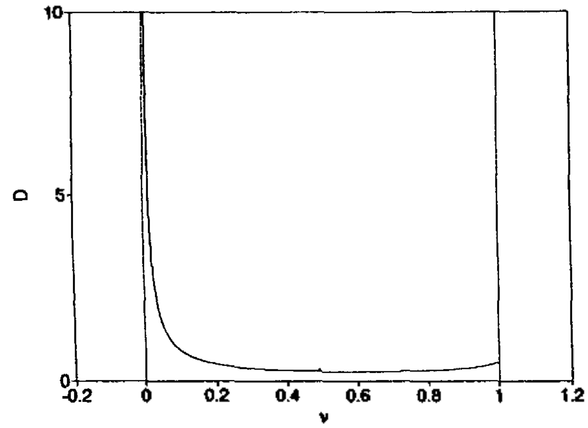

Figure 3. The phase diagram between ν and diffusion coefficient by taking $\beta=1$.

and becomes divergent at $x=0$. For $x<0$ the probability simply increases as $|x|$ decreases and is proportional to $1/|x|^{2\nu D}$ approximately for $|x|\ll 1$ (See Figure 2). The divergence is caused by the multiplicative noise and is independent of the deterministic term. The main interesting phenomena occurs in the region $x>0$. Thus, from now on we shall restrict ourselves to this region. The stochastic phenomena are completely different from the previous case, since the noise induces phase transitions. At the critical point $V(x)$ and its first derivative with respect to x become zero. Thus, the critical values of x are

$$x_c=0,\ \frac{2\beta(1-\nu_c)}{3-2\nu_c} \tag{14}$$

The first case is trivial and let us neglect it. Then, the relation between the critical values of diffusion coefficient and ν is

$$D_c=\frac{1}{2\nu_c}\left(\frac{\beta}{3-2\nu_c}\right)^{3-2\nu_c}(2-2\nu_c)^{2-2\nu_c} \tag{15}$$

The bifurcation phase diagram in the $\nu-D$ plane is shown in Figure 3. The straight lines $\nu=0$ and $\nu=1$ show the pitchfork bifurcation different from the saddle-node bifurcation obtained from Eq. (15). The line $\nu=0$ is solely due to the multiplicative noise, while the $\nu=1$ line is due to the coupling between the noise and the linear part of deterministic term. The variation of the probability distributions by crossing the straight lines are shown in Figures 4(a) and 4(b). As shown in the figures, the variation of the probability distribution is discontinuous. Let us discuss the probability distributions by the saddle-node bifurcation. We change the value of diffusion coefficient first by keeping $\nu=\nu_c=0.5$. The critical value of diffusion coefficient is $D=0.25$. Below the critical value the coupling between the noise and deterministic terms is very important. Thus, the probability distribution has a maximal and minimal peaks satisfying the condition in Eq. (13). Of course, at $x=0$ the divergence occurs due to the noise term. As the value of D increases, the effect of the coupling decreases and the noise itself becomes more important. Above the critical value the effect of the coupling may be neglected compared with the noise effect. An example is given in Figure 5(a). The probability distributions in

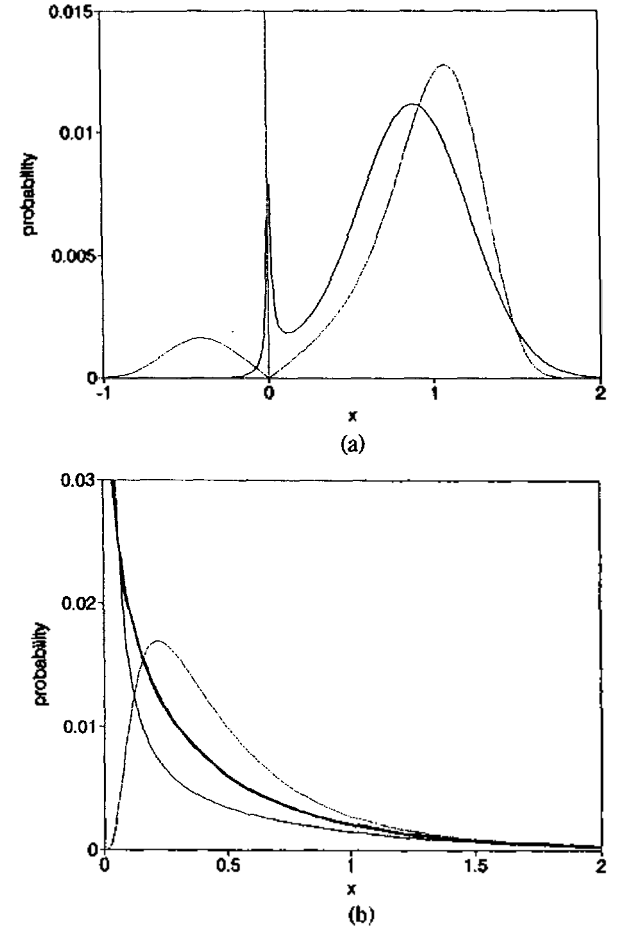

Figure 4. (a) The variation of the probability when the system crosses the line $\nu=0$ along the line $D=0.1$ by taking $\beta=1$. The dotted and solid curves express $\nu=-0.5$ and 0.5, respectively; (b) The variation of the probability when the system undergoes the pitchfork bifurcation by crossing the line $\nu=1$ along the line $D=0.6$ by taking $\beta=1$. The dotted, heavy solid, and solid curves show $\nu=1.2$, 1, and 0.8, respectively.

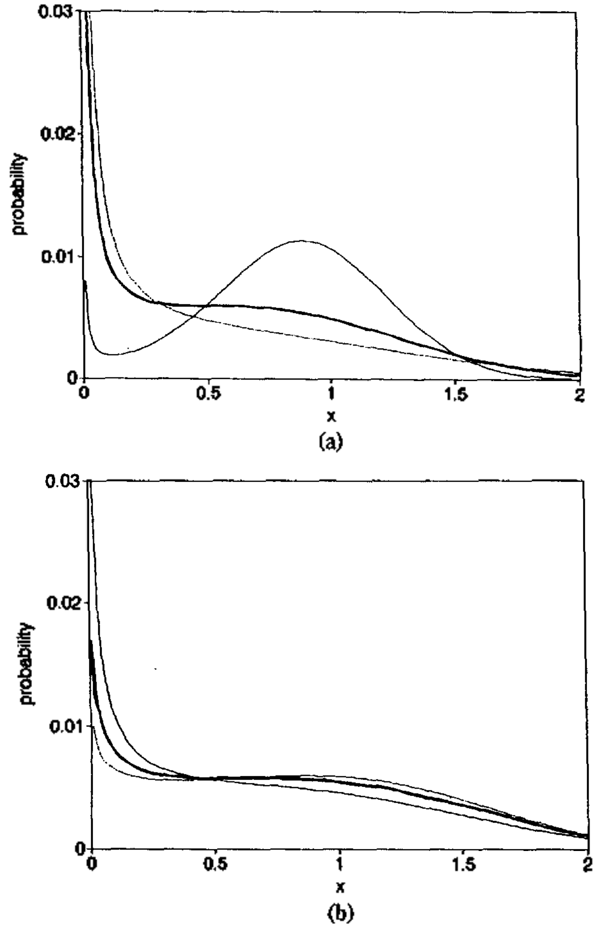

Figure 5. (a) The variation of the probability when the system undergoes saddle-node bifurcation along the line $\nu=0.5$ by taking $\beta=1$. The dotted, heavy solid, and solid curves indicate $D=0.5$, 0.25, and 0.1, respectively; (b) The variation of the probability when the system undergoes saddle-node bifurcation along the line $D=0.5$ by taking $\beta=1$. The dotted, heavy solid, and solid curves indicate $\nu=0.1$, 0.3, and 0.172, respectively.

the case of the constant D and changing ν are shown in Figure 5(b). In this case the critical values of D and ν are 0.5 and approximately 0.172, respectively. The phenomena of this case is the same as the previous example. Thus, the variation of the probability distributions by the saddle-node bifurcation is continuous.

Now, let us turn to the stationary probability distribution with the aid of the FPE based on the Stratonovich theory. The probability distribution can be easily obtained from Eq. (7b).

$$P_S(x)=A\ \exp\{-V(x)/D\} \tag{16}$$

where the subscript S denotes the Stratonovich probability distribution and

$$V(x)=\begin{cases} \dfrac{1}{3-2\nu}|x|^{3-2\nu}\mp\dfrac{\beta}{2(1-\nu)}|x|^{2-2\nu}+\nu D\ \ln|x| & \text{for } \nu\neq 1 \text{ and } 1.5, \\ |x|+(D\mp\beta)\ \ln|x| & \text{for } \nu=1, \\ \left(1+\dfrac{3D}{2}\right)\ \ln|x|\pm\dfrac{\beta}{|x|} & \text{for } \nu=1.5. \end{cases} \tag{17}$$

The above result corresponds to the result obtained by replacing $2\nu D$ in Eq. (9) by νD. In the previous paper[2] we have compared the effects of the parameters on the probability distributions obtained by the Ito and Stratonovich methods for the Schlögl model with the first order transition in detail. We may directly apply the results to the present case and thus refer the detailed discussion to the previous paper.

Escape Rate

Let us discuss the dynamic behaviors of the system which is governed by the Langevin equation given in Eq. (6). The multiplicative random force may have great influence on the dynamic behaviors as well as the stationary behaviors. Unfortunately. The explicit time-dependent solution of the FPE with nonlinear drift and nonconstant diffusion terms is not available. When diffusion coefficient is very small, the dynamic behaviors are approximately expressed by the stationary state. The escape rate is one of the examples. Introducing a new variable y as

$$y=\begin{cases} |x|^{1-\nu} & \text{for } x>0, \\ -|x|^{1-\nu} & \text{for } x<0, \end{cases} \tag{18}$$

the Langevin equation reduces to

$$\frac{dy}{d\tau}=f(y)+(1-\nu)\xi(\tau) \tag{19}$$

where

$$f(y)=(1-\nu)(\beta y\mp y^{(2-\nu)/(1-\nu)}), \tag{20}$$

The upper and lower signs in the above expression correspond to the cases $y>0$ and $y<0$, respectively. When $\nu<1$, y goes to zero as $x\to 0$. In the case that $\nu>1$, y becomes infinity as x goes to zero. The value $\nu=1$ is also very important in the dynamic phenomena, as shown later. The corresponding FPE is

$$\frac{\partial}{\partial\tau}P(y,\tau)=-\frac{\partial}{\partial y}[f(y)P(y,\tau)]+(1-\nu)^2D\frac{\partial^2}{\partial y^2}P(y,\tau)$$
$$=-\frac{\partial}{\partial y}S(y,\tau) \tag{21}$$

where $S(y,\tau)$ is the probability current.

Let us consider the fluctuating intermediate near the point $y_{min}=\beta^{+2\nu}$, which is the stable steady state of the original system. Then, the system escapes from the state by crossing the unstable steady state, which is the top of the potential barrier. Let us assume that as soon as the system crosses the top, it escapes from the state. Thus, we may consider only the case $x>0$, approximately. The escape rate is defined as the probability current from the stable steady state to the unstable steady state per the probability near the stable steady state, that is,

$$r_\nu=(1-\nu)^2D\Big[\int_{y_1}^{y_2}\exp\Big\{-\frac{V(y)}{(1-\nu)^2D}\Big\}dy$$
$$\times\int_{y_{min}}^{0-\delta}\exp\Big\{\frac{V(y)}{(1-\nu)^2D}\Big\}dy\ \Big]^{-1}, \tag{22}$$

where y_1 and y_2 are the values of y near y_{min}, δ is an infinitesimally small number and $V(y)$ is

$$V(y)=\int^y f(y')\ dy' \tag{23}$$

Using the method of the steepest descent, the escape rate is[6]

$$r_\nu\simeq\frac{2}{\pi}(1-\nu)^{1/2}\beta\ \exp\Big\{-\frac{\beta^{3-2\nu}}{2D(3-2\nu)(1-\nu)}\Big\}. \tag{24}$$

Let us define the escape rate at $\nu=0$ as r_0. The ratio is

$$\frac{r_\nu}{r_0}=(1-\nu)^{1/2}\ \exp\Big\{-\frac{\beta^3}{2D}\Big[\frac{1}{\beta^{2\nu}(3-2\nu)(1-\nu)}-\frac{1}{3}\Big]\Big\} \tag{25}$$

We may easily discuss the effect of multiplicative noise on the escape rate from the ratio. Figures 6(a) and 6(b) show the effects of the parameters on the ratio. It is obvious that the ratio increases in $\nu<0$ and decreases in $0<\nu<1$, when the diffusion coefficient at a constant β increases. At a fixed diffusion coefficient the ratio for small values β is similiar to the case of the variation of the diffusion coefficients. However, as β increases the ratio becomes quite different from that for small β since the exponential function has a minimum value for the large β. The most important case is that the escape rate vanishes as ν approaches to 1. That is, it is impossible that the system escapes the potential barrier of $\nu\geq 1$. This means that $\nu=1$ is a critical dynamic exponent. This can be easily confirmed by the relaxation time.[8]

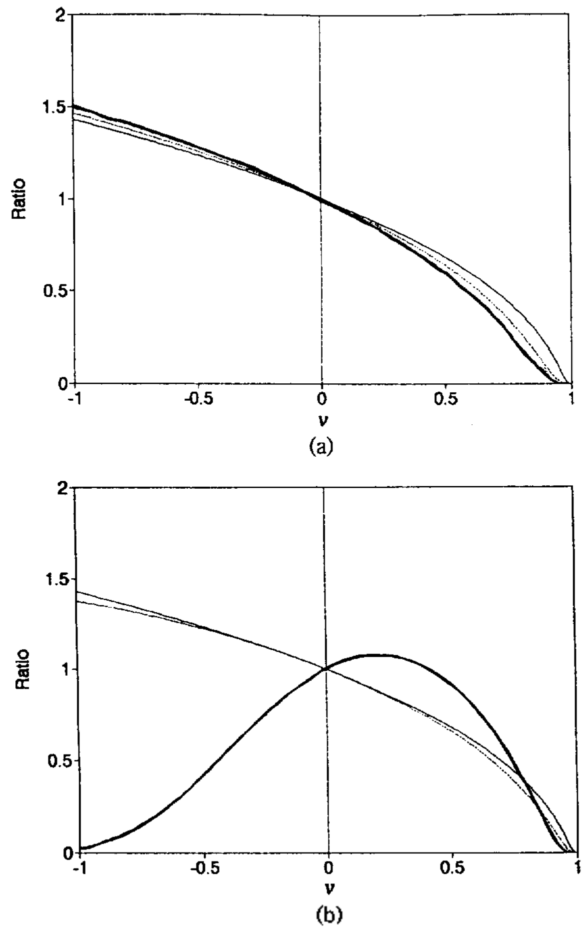

Figure 6. (a) Dependence of the escape rate on the diffusion coefficient when $\beta=1$. The solid, dotted, and heavy solid curves denote $D=0.1$, 0.3, and 0.5, respectively; (b) Dependence of the escape rate on β when $D=0.1$. The solid, dotted, and heavy solid curves indicate $\beta=1$, 2, and 4, respectively.

Conclusion and Discussion

We have discussed some stochastic phenomena for the Schlögl model subjected to a multiplicative random force, which is singular at the deterministic unstable steady state. Let us point out some important results including the previous results.[1,2]

(A) The multiplicative noise $|x|^\nu\ \xi(\tau)$ has an attracting (repelling) effect as $\nu>0$ ($\nu<0$), that is, it attracts (repels) the probability toward (away from) the unstable steady state. As $|\nu|$ increases, the attracting (repelling) force increases. The property competes with deterministic term in determining the stochastic properties of the system.

(B) When $\nu>0$, the stationary probability distribution becomes divergent at $x=0$. This result is clearly not realistic. Thus, a more realistic stochastic model should be proposed.

(C) In the region $x>0$ the straight lines $\nu=0$ and $\nu=1$ give marginal situation, that is, the fluctuating intermediate undergoes the pitchfork bifurcation by crossing the lines and thus the variation of probability distributions becomes discontinuous, when the system undergoes the pitchfork phase transition.

(D) When a system has the same multiplicative noise and linear part of deterministic term, the same pitchfork bifurcations occur.[1,2,7] The reason is that $\nu=0$ and $\nu=1$ lines are due to the noise and coupling between noise and linear part, respectively.

(E) The diffusion coefficient with ν induces the saddle-node bifurcation in the case of $x>0$ and $0<\nu<1$. Below the curve of the saddle-node bifurcation the coupling between the drift and noise terms plays the most important role. However, the multiplicative noise term becomes dominant above the curve. Thus, it is clear that the variation of probability distributions is continuous.

(E) It should be very careful to apply the Ito or Stratonovich FPE to an actual system.[2]

(F) $\nu=1$ is the critical dynamic exponent. At $\nu\geq1$ it is impossible that the intermediate for the Schlögl model with the second order transition near the stable steady state escapes over the unstable steady state of the potential barrier. For the model with the first order transition the transition rate from one stable steady state to the other stable state through the unstable state become zero,[1] if $\nu\geq1$. Also, the relaxation time for the models becomes infinite when $\nu=1$.[1]

Some of the above results are unrealistic. Maybe the multiplicative noise should be expressed by a polynomial of the concentration of the intermediate instead of $|x|^{\nu}$. The reason is that starting from the master equation for the Schlögl model, the diffusion term in the FPE is expressed in terms of a polynomial of concentration.[5] Investigation on this aspect is in progress in our group.

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Study of the Nonstoichiometry and Physical Properties of the $Nd_{1-x}Sr_xFeO_{3-y}$ System

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The nonstoichiometric perovskite solid solutions of the $Nd_{1-x}Sr_xFeO_{3-y}$ system for the compositions of $x=0.00$, 0.25, 0.50, 0.75, and 1.00 have been prepared at 1150℃ in the air pressure. The compound of $x=0.00$, $NdFeO_{3.0}$, contains only Fe^{3+} ion in octahedral site and the others involves the mixed valence state between Fe^{3+} and Fe^{4+} ions. The mole ratio of Fe^{4+} ion or the τ-value increases steadily with the x-value and then is maximized at the composition of $x=1.00$. The nonstoichiometric chemical formulas of the system are formulated from the x, τ, and y values. From the Mössbauer spectroscopy, the isomer shift of Fe^{3+} ion decreases with the increasing x-value, which is induced by the electron transfer between the Fe^{3+} and Fe^{4+} ions. The transfer is made possible by the indirect interaction between Fe^{3+} and Fe^{4+} ions *via* the oxygen ion. The e_g electrons of the Fe^{3+} ions are delocalized over all the Fe ions. Due to the electron transfer, the activation energy of electrical conductivity is decrease with the increasing amount of Fe^{4+} ion.

Introduction

In the perovskite-type ABO_3 compound, the transition metal placed in B-site is able to have higher valence state which is generally stabilized with a large A-site ion. The perovskite-type compounds have been studied extensively because of