A Theoretical Investigation of Nonlinear Chemical Reactions Near the Critical Point in the Presence of Diffusion

Seokmin Shin, and Kook Joe Shin*

Department of Chemistry, Seoul National University, Seoul 151

Received April 7, 1986

A nonlinear analysis is presented for the treatment of fluctuations near the critical point in the presence of diffusion in the Schlögl models. The two time scaling method is used to obtain an evolution equation for the amplitude of fluctuations. It is shown that the fluctuations decay to zero in the stable region and they are enhanced to a finite value as time goes to infinity in the unstable region.

Introduction

In recent years, much attention has been paid to the instabilities and transition phenomena that may appear in chemical systems subject to nonequilibrium constraints. These far-from-equilibrium instabilities and nonequilibrium transitions are observed in many fields.[1-5] The close analogy between the so-called "chemical instabilities" and equilibrium phase transitions has been particularly stressed.[6-9] Indeed, both kinds of transitions are characterized by an enhancement of fluctuations, long-range order, and critical slowing down.

In this paper, we focus attention on transitions in nonequilibrium chemical systems characterized by multiple homogeneous steady states. The typical examples we choose for our study are two Schlögl models. The relaxations of these chemical systems from the unstable steady state in the homogeneous situation have been widely studied by many authors.[10-12] They have obtained the approximate probability distribution function satisfying the Fokker-Planck equation. In the presence of diffusion we may also obtain the probability distribution.[11,13] Yet the diffusion can change the stability property of the homogeneous steady states. The reaction-diffusion systems give rise to solutions with variety of characteristics arising via a bifurcation mechanism far from thermodynamic equilibrium.[14,15] So we can analyze the dynamic behaviors of these chemical systems, stability property and fluctuations, instead of obtaining the probability distribution.

The purpose of this paper is to discuss the effect of nonlinear terms on fluctuations of intermediates in the Schlögl models near the critical point caused by diffusion. This kind of nonlinear dynamic phenomena can be studied only by approximate methods. The method to be used here is the two time scaling method.[16-18] In the two time scaling method the whole range of time is divided into three regions of time. The initial region of time is the range of time where the linear approximation is valid. The second region is the region in which the nonlinear effect becomes important and the system approaches a steady state. The final region is the region where the system stays at the steady state.

In the present paper, we analyze the two Schlögl models separately. First we consider the linear case and then the nonlinear case is studied using the two time scaling method. After that we discuss the resulting evolution equation for the amplitude of fluctuations. Finally, the main conclusions and some remarks are given.

Theory

A. Schlögl's First Model

The first type of Schlögl model considered here is

$$\begin{aligned} A+X &\rightleftharpoons 2X \\ B+X &\rightleftharpoons C \end{aligned} \tag{1}$$

The concentration of reacting intermediate $X(\vec{r},t)$ satisfies the following rate expression:

$$\frac{\partial X(\vec{r},t)}{\partial t}=D\nabla^2 X(\vec{r},t)+F[X(\vec{r},t)] \tag{2}$$

where

$$F[X(\vec{r},t)]=\alpha X(\vec{r},t)-\beta X(\vec{r},t)^2+\lambda(\vec{r},t) \tag{3}$$

Here α and β are assumed to be positive constants, λ is a pumping parameter. This quadratic model is known to exhibit a second order phase transition.

The homogeneous steady states of this system are determined by the solution of the equation $F(X^0_{st}, \lambda^0_{st}) = 0$.

$$\alpha X^\circ_{st}-\beta X^{\circ 2}_{st}+\lambda^\circ_{st}=0 \tag{4}$$

$$X^\circ_{st}=\frac{1}{2\beta}\left(\alpha\pm\sqrt{\alpha^2+4\beta\lambda^\circ_{st}}\right) \tag{5}$$

When there is no diffusion (*i.e.* homogeneous state), from the linear stability analysis it is well known that the steady state is on the stable branch if the first order derivative of λ^0_{st} with respect to X^0_{st} is positive and it is on the unstable branch if the derivative is negative. At the marginal stability point the derivative vanishes.

In order to consider the fluctuation around a steady state we expand eq.(2) in terms of $x\equiv X-X^0_{st}$. Then we obtain, for the case of $\lambda=\lambda^\circ_{st}$,

$$\frac{\partial x(r,t)}{\partial t}=(\alpha-2\beta X^\circ_{st})x(r,t)-\beta x(r,t)^2+D\frac{\partial^2 x(r,t)}{\partial r^2} \tag{6}$$

Here we consider only one-dimensional diffusion and r is the one-dimensional spatial variable.

(A.1) Linear Case and Stability Analysis

Neglecting the quadratic term in eq. (6), we have a linear equation for x.

$$\frac{\partial x}{\partial t} = (\alpha - 2\beta X^{\circ}_{st})x + D\frac{\partial^2 x}{\partial r^2} \tag{7}$$

If we assume a solution of the form $x = x_o e^{at} \cos kr$, the exponent a is given by

$$a = \alpha - 2\beta X^{\circ}_{st} - Dk^2 \tag{8a}$$

$$= \mp\sqrt{\alpha^2 + 4\beta\lambda^{\circ}_{st}} - Dk^2 \tag{8b}$$

The stability of the solution is determined by the sign of the exponent a. (Here we assume a non-periodic solution, so a must be real). Thus, the system can be stable or unstable depending on the controllable variables λ^0_{st} and k^2. The conditions for the linear stability are

$$\alpha^2 + 4\beta\lambda^{\circ}_{st} \geq 0 \qquad (a \text{ is real}) \tag{9}$$

$$\mp\sqrt{\alpha^2 + 4\beta\lambda^{\circ}_{st}} < Dk^2 \qquad (a \text{ is negative}) \tag{10}$$

We notice that at the homogeneous stable branch ($X^0_{st} > \frac{\alpha}{2\beta}$) the two conditions are satisfied. At the homogeneous unstable branch ($X^0_{st} < \frac{\alpha}{2\beta}$) the system can become stable if k^2 has a value larger than the critical value k_c^2 when λ^0_{st} is fixed. The division between the stable and unstable regions in (k^2, λ^0_{st})-space is depicted in Figure 1.

If we let $\lambda^0_{st} = 0$, then the steady state $X^0_{st} = \alpha/\beta$ has exponent whose value is $a = -\alpha - Dk^2 < 0$, so this steady state is also stable in the presence of diffusion. Yet for the steady state $X^0_{st} = 0$, the exponent a becomes $\alpha - Dk^2$ which can have both signs depending on the value of k^2. In other words, there is a critical value k_c^2 upon which the stability property of the system changes. The critical value is given by

$$k_c^2 = \alpha/D \tag{11}$$

If $k^2 > k_c^2$, the system is (linearly) stable ($a < 0$), and if $k^2 < k_c^2$, it is unstable ($a > 0$).

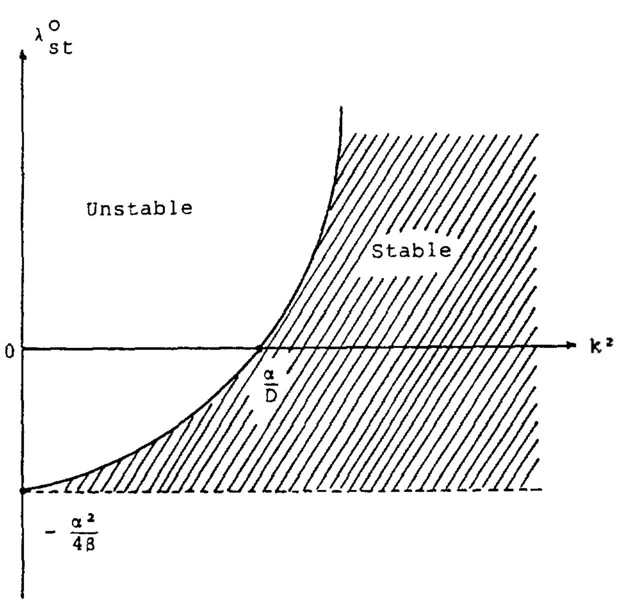

Figure 1. Stability diagram resulting from eqs. (9) and (10).

Using the value of k_c^2, the exponent a can be written as

$$a = \alpha - Dk^2 = -D(k^2 - k_c^2) \tag{12}$$

The solution in the linear case is

$$x(r, t) = x_o \exp[-D(k^2 - k_c^2)t]\cos kr \tag{13}$$

The region to be considered in this paper is near the critical point. In the critical region where $k^2 \cong k_c^2$, eq. (13) becomes

$$x(r, t) \cong x_o \cos kr \tag{14}$$

(A.2) Nonlinear Case

The linear theory predicts stability for $k^2 > k_c^2$, and instability for $k^2 < k_c^2$. For $k^2 < k_c^2$, the fluctuation will grow exponentially in time with a growth rate proportional to $k_c^2 - k^2$. Clearly, this exponentially growing solution according to the linear theory, cannot represent the actual solution for very long, for it will soon grow sufficiently large so that the nonlinear terms become important. Then a nonlinear analysis becomes necessary.

In our nonlinear analysis, we shall apply the two time scaling method. The whole range of time is divided into three regions. The initial region of time denoted by τ_0 is conventionally the range of time where the linear approximation is valid. In the present analysis, however, we shall include a slight nonlinear effect to obtain more accurate solution. The second region, denoted by τ_1, is one in which the nonlinear effects become important, and the solution continues to evolve in time until it approaches the steady state which is the third region, reached in the limit as τ_1 becomes infinite.

Let us scale the time and the fluctuation x as

$$\tau_m = \varepsilon^{2m} t \ , \quad m = 0, 1$$
$$x = \sum_i \varepsilon^i x_i, \quad i = 1, 2 \tag{15}$$

where ε is a parameter to be defined later. In the initial region of time, the eq.(6) for the steady state $X^0_{st} = 0$ becomes

$$\frac{\partial x}{\partial t} = D\frac{\partial^2 x}{\partial r^2} + \alpha x - \beta x^2 \quad (\alpha = Dk_c^2) \tag{16}$$

Each term in the above equation can be scaled, using the scaling scheme of eq.(15), as follows:

$$\frac{\partial x}{\partial t} \rightarrow \varepsilon\frac{\partial x_1}{\partial \tau_o} + \varepsilon^2\frac{\partial x_2}{\partial \tau_o} \tag{17}$$

$$(\alpha + D\frac{\partial^2}{\partial r^2})x \rightarrow \varepsilon(\alpha + D\frac{\partial^2}{\partial r^2})x_1 + \varepsilon^2(\alpha + D\frac{\partial^2}{\partial r^2})x_2 \tag{18}$$

$$-\beta x^2 \rightarrow -\varepsilon^2\beta x_1^2 + O(\varepsilon^3) \tag{19}$$

For the first order of ε, we obtain

$$\frac{\partial x_1}{\partial \tau_o} = (\alpha + D\frac{\partial^2}{\partial r^2})x_1 \tag{20}$$

which is just the linear equation already discussed. Then,

$$x_1 \cong x_0 \cos kr \tag{21}$$

in the critical region ($k \cong k_c$). For the second order of ε the following equation is obtained.

$$\begin{aligned}\frac{\partial x_2}{\partial \tau_0} &= (\alpha + D\frac{\partial^2}{\partial r^2})x_2 - \beta x_1^2 \\ &= (\alpha + D\frac{\partial^2}{\partial r^2})x_2 - \frac{\beta x_0^2}{2}(1+\cos 2kr)\end{aligned} \tag{22}$$

x_2 represents the correction of the order ε^2 due to the nonlinear effect.

We assume that fluctuations depend on τ_0 and τ_1 through the amplitude of fluctuations, x_0. That is,

$$x(r, \tau_0, \tau_1) = x_0(\tau_0, \tau_1)\cos kr \tag{23}$$

in the critical region. From eqs. (21) and (23) we find that x_0 is approximately independent of τ_0 in the critical region. That is, $x_0(\tau_0, \tau_1) \cong x_0(\tau_1)$. Therefore, x_1 is dependent only on τ_1 through $x_0(\tau_1)$ via eq. (21). Since x_2 is the second correction to x, we may also assume that x_2 is independent of τ_0. Then we let $\partial x_2/\partial \tau_0 = 0$ in eq. (22), which gives

$$(\alpha + D\frac{\partial^2}{\partial r^2})x_2 = \frac{\beta x_0(\tau_1)^2}{2}(1+\cos 2kr) \tag{24}$$

From eq. (24) we have the particular solution for x_2 as

$$x_2 = \frac{\beta}{6\alpha}x_0(\tau_1)^2(3-\cos 2kr) \tag{25}$$

The resulting solution (corrected solution) in the initial region of time is

$$\begin{aligned}x(r, \tau_1) &= \varepsilon x_0(\tau_1)\cos kr \\ &\quad + \varepsilon^2\frac{\beta}{6\alpha}x_0(\tau_1)^2(3-\cos 2kr)\end{aligned} \tag{26}$$

in the critical region ($k \cong k_c$). The solution is more accurate than the linear case in the sense that a slight nonlinear effect is included.

Since we are examining the stability of $X_n^0 = 0$ in the neighborhood of $k = k_c$, it is natural to expand the solution about this quantity. Therefore, we define ε by the relationship

$$\varepsilon^2 = |k^2 - k_c^2| \tag{27}$$

The parameter ε is thus a measure of the nearness of k^2 to k_c^2.

Substituting eq. (26) and scaling time τ_1 into eq. (16), we obtain, in the second region of time,

$$\begin{aligned}\frac{\partial x}{\partial t} &\rightarrow \varepsilon^2\frac{\partial x}{\partial \tau_1} \\ &= \varepsilon^3\left(\frac{dx_0(\tau_1)}{d\tau_1}\right)\cos kr + O(\varepsilon^4)\end{aligned} \tag{28}$$

$$\begin{aligned}(\alpha + D\frac{\partial^2}{\partial r^2})x &\rightarrow (\alpha + D\frac{\partial^2}{\partial r^2})(\varepsilon x_1 + \varepsilon^2 x_2) \\ &= \varepsilon\alpha x_0(\tau_1)\cos kr + \varepsilon^2\frac{\beta}{6}x_0(\tau_1)^2(3-\cos 2kr) \\ &\quad - \varepsilon Dk^2 x_0(\tau_1)\cos kr + \varepsilon^2 Dk^2\frac{2\beta}{3\alpha}x_0(\tau_1)^2\cos 2kr\end{aligned} \tag{29}$$

Using the relation

$$\begin{aligned}k^2 &= (k^2 - k_c^2) + k_c^2 \\ &= \eta'\varepsilon^2 + k_c^2\end{aligned} \tag{30}$$

where

$$\eta' = \begin{cases} +1 & \text{if } k^2 > k_c^2 \\ -1 & \text{if } k^2 < k_c^2\end{cases}$$

eq. (29) becomes

$$\begin{aligned}&(\alpha + D\frac{\partial^2}{\partial r^2})x \\ &\rightarrow \varepsilon\alpha x_0(\tau_1)\cos kr + \varepsilon^2\frac{\beta}{6}x_0(\tau_1)^2(3-\cos 2kr) \\ &- \varepsilon Dk_c^2 x_0(\tau_1)\cos kr - \varepsilon^3\eta' D\, x_0(\tau_1)\cos kr \\ &+ \varepsilon^2\frac{2\beta}{3}x_0(\tau_1)^2\cos 2kr + \varepsilon^4\frac{2\beta\eta' D}{3\alpha}x_0(\tau_1)^2\cos 2kr \\ &= \varepsilon^2\frac{\beta}{2}x_0(\tau_1)^2(1+\cos 2kr) \\ &- \varepsilon^3\eta\, x_0(\tau_1)\cos kr + O(\varepsilon^4)\end{aligned} \tag{31}$$

where

$$\eta = \begin{cases} D & \text{if } k^2 > k_c^2 \\ -D & \text{if } k^2 < k_c^2\end{cases} \tag{32}$$

Finally,

$$\begin{aligned}-\beta x^2 &\rightarrow -\varepsilon^2\beta x_0(\tau_1)^2\cos^2 kr \\ &\quad - \varepsilon^3\frac{\beta^2}{3\alpha}x_0(\tau_1)^3(\cos kr)(3-\cos 2kr) + O(\varepsilon^4) \\ &= -\varepsilon^2\frac{\beta}{2}x_0(\tau_1)^2(1+\cos 2kr) \\ &\quad - \varepsilon^3\frac{\beta^2}{6\alpha}x_0(\tau_1)^3(5\cos kr + \cos 3kr) + O(\varepsilon^4)\end{aligned} \tag{33}$$

From eqs. (28), (31), and (33), taking terms up to the third order in ε, we have

$$\begin{aligned}&\left(\frac{dx_0(\tau_1)}{d\tau_1}\right)\cos kr \\ &= -\eta x_0(\tau_1)\cos kr - \frac{\beta^2}{6\alpha}x_0(\tau_1)^3(5\cos kr + \cos 3kr)\end{aligned} \tag{34}$$

Using the orthogonality condition of cosine functions, the following equation is obtained:

$$\frac{dx_o(\tau_1)}{d\tau_1} = -\eta x_o(\tau_1) - \frac{5\beta^2}{6\alpha} x_o(\tau_1)^3 \tag{35}$$

B. Schlögl's Second Model

The second Schlögl model is given by

$$\begin{aligned} A+2X &\rightleftharpoons 3X \\ B+X &\rightleftharpoons C \end{aligned} \tag{36}$$

In this case the rate expression is

$$F[X(\vec{r},t)] = \alpha X(\vec{r},t) - \beta X(\vec{r},t)^3 + \lambda(\vec{r},t) \tag{37}$$

Again, the homogeneous steady states of this system are determined by the solution of the equation $F(X^0_{st}, \lambda^0_{st}) = 0$. The relationship between X^0_{st} and λ^0_{st} is

$$\lambda^{\circ}_{st} = -\alpha X^{\circ}_{st} + \beta X^{\circ 3}_{st} \tag{38}$$

This cubic model shows two stable steady state branches and one unstable branch and exhibits a first order phase transition.

The expansion of the rate equation in terms of $x = X - X^0_{st}$ results in, for the cases of $\lambda = \lambda^0_{st}$,

$$\frac{\partial x(r,t)}{\partial t} = (\alpha - 3\beta X^{\circ 2}_{st})x - 3\beta X^{\circ}_{st} x^2 - \beta x^3 + D\frac{\partial^2 x}{\partial r^2} \tag{39}$$

(B.1) Linear Case and Stability Analysis

Taking only the linear terms in eq. (39), we get

$$\frac{\partial x}{\partial t} = (\alpha - 3\beta X^{\circ 2}_{st})x + D\frac{\partial^2 x}{\partial r^2} \tag{40}$$

As in the previous analysis, we assume a solution of the form $x = x_0 e^{at} \cos kr$, then a is given by

$$a = \alpha - 3\beta X^{\circ 2}_{st} - Dk^2 \tag{41}$$

Now consider the case of $\lambda^0_{st} = 0$. For the steady states $X^0_{st} = \pm\sqrt{\alpha/\beta}$, the value of a becomes $a = -2\alpha - Dk^2$ which is always negative when α is positive. Therefore, the two steady states preserve their stability in the presence of diffusion. Yet the homogeneous unstable steady state $X^0_{st} = 0$ has $a = \alpha - Dk^2$. So it has the same property as the state $X^0_{st} = 0$ in the previous model. Therefore there is a critical point $k_c^2 = \alpha/D$. If $k^2 > k_c^2$, the steady state $X^0_{st} = 0$ becomes stable.

The linear equation for $X^0_{st} = 0$ is

$$\frac{\partial x}{\partial t} = \alpha x + D\frac{\partial^2 x}{\partial r^2} \tag{42}$$

This is the same form as in the previous model. So the solution in the linear case is

$$x(r,t) = x_o \exp[-D(k^2 - k_c^2)t] \cos kr \tag{43}$$

which becomes, in the critical region,

$$x(r,t) \cong x_o \cos kr \tag{44}$$

(B.2) Nonlinear Case

We apply the same scaling scheme as before:

$$\begin{aligned} \tau_m &= \varepsilon^{2m} t \quad, \; m=0,\ 1 \\ x &= \sum_i \varepsilon^i x_i \;,\; i=1,\ 2 \end{aligned} \tag{45}$$

First, in the initial region of time, the equation of motion for the steady state $X^0_{st} = 0$ becomes

$$\frac{\partial x}{\partial t} = D\frac{\partial^2 x}{\partial r^2} + \alpha x - \beta x^3 \tag{46}$$

Each term can be scaled as before:

$$\frac{\partial x}{\partial t} \rightarrow \varepsilon\frac{\partial x_1}{\partial \tau_o} + \varepsilon^2\frac{\partial x_2}{\partial \tau_o} \tag{47}$$

$$(\alpha + D\frac{\partial^2}{\partial r^2})x \rightarrow \varepsilon(\alpha + D\frac{\partial^2}{\partial r^2})x_1 + \varepsilon^2(\alpha + D\frac{\partial^2}{\partial r^2})x_2 \tag{48}$$

$$-\beta x^3 \rightarrow O(\varepsilon^3) \tag{49}$$

The first order terms in ε gives the linear equation

$$\frac{\partial x_1}{\partial \tau_o} = (\alpha + D\frac{\partial^2}{\partial r^2})x_1 \tag{50}$$

whose solution is

$$x_1 \cong x_o(\tau_1) \cos kr \tag{51}$$

For the second order of ε

$$\frac{\partial x_2}{\partial \tau_o} = (\alpha + D\frac{\partial^2}{\partial r^2})x_2 \tag{52}$$

Following the argument already discussed, we can set $\partial x_2/\partial \tau_0 = 0$. This gives $x_2 = 0$. This means that there is no correction resulting from nonlinear effect up to the order ε^2. Therefore, the solution in the initial region of time is

$$x(r,\tau_1) = \varepsilon x_o(\tau_1) \cos kr \tag{53}$$

Now, in the second region of time, each term in eq. (46) can be scaled as before:

$$\begin{aligned} \frac{\partial x}{\partial t} &\rightarrow \varepsilon^2 \frac{\partial x}{\partial \tau_1} \\ &= \varepsilon^3 [\frac{dx_o(\tau_1)}{d\tau_1}] \cos kr \end{aligned} \tag{54}$$

$$\begin{aligned} (\alpha + D\frac{\partial^2}{\partial r^2})x &\rightarrow \varepsilon(\alpha + D\frac{\partial^2}{\partial r^2})x_o(\tau_1) \cos kr \\ &= \varepsilon\alpha x_o(\tau_1)\cos kr - \varepsilon Dk^2 x_o(\tau_1)\cos kr \\ &= \varepsilon\alpha x_o(\tau_1)\cos kr - \varepsilon Dk_c^2 x_o(\tau_1)\cos kr \\ &\quad - \varepsilon^3\eta\, x_o(\tau_1)\cos kr \end{aligned}$$

$$= -\varepsilon^3 \eta \; x_o(\tau_1) \cos kr \tag{55}$$

where

$$\eta = \begin{cases} D & \text{if } k^2 > k_c^2 \\ -D & \text{if } k^2 < k_c^2 \end{cases} \tag{56}$$

$$\begin{aligned} -\beta x^3 \to & -\varepsilon^3 \beta \; x_o(\tau_1)^3 \cos^3 kr \\ & = -\varepsilon^3 \frac{\beta}{4} x_o(\tau_1)^3 \; (3 \cos kr + \cos 3kr) \end{aligned} \tag{57}$$

From eqs. (54), (55), and (57) we obtain

$$\begin{aligned} \frac{dx_o(\tau_1)}{d\tau_1} \cos kr = & -\eta \; x_o(\tau_1) \cos kr \\ & - \frac{\beta}{4} x_o(\tau_1)^3 (3 \cos kr + \cos 3kr) \end{aligned} \tag{58}$$

The final equation for evolution of $x_0(\tau_1)$ is

$$\frac{dx_o(\tau_1)}{d\tau_1} = -\eta \; x_o(\tau_1) - \frac{3\beta}{4} x_o(\tau_1)^3 \tag{59}$$

C. Evolution of Fluctuations

The evolution equations of the amplitude of fluctuations $x_0(\tau_1)$ in the two Schlögl models can be written as

$$\frac{dx_o(\tau_1)}{d\tau_1} = -\eta \; x_o(\tau_1) - \delta x_o(\tau_1)^3 \tag{60}$$

where $\eta = \pm D$ for $k^2 \gtrless k_c^2$, and

$$\delta = \begin{cases} \dfrac{5\beta^2}{6\alpha} & \text{for the first (quadratic) model} \\ \dfrac{3}{4}\beta & \text{for the second (cubic) model} \end{cases} \tag{61}$$

Notice that δ is always positive since $\alpha > 0$, $\beta > 0$. Yet the coefficient η can be positive or negative. If $\eta > 0$, the system has a stable steady state corresponding to $x_0 = 0$ and approaches the stable steady state as time goes to infinity. In the case that η is negative, $\pm(\eta/\delta)^{1/2}$ correspond to stable steady states and $x_0 = 0$ is an unstable steady state. The amplitude of fluctuations approaches the stable steady states as τ_1 goes to infinity.

The above properties can be seen if we look at the deterministic solution of eq. (60). It reads

$$\begin{aligned} x_o(\tau_1) = & x_o(0) \exp(-\eta \tau_1) \\ & /[1 + x_o(0)^2 (\delta/\eta)(1 - \exp(-2\eta\tau_1))]^{1/2} \end{aligned} \tag{62}$$

For $\eta > 0$, as $\tau_1 \to \infty$

$$\lim_{\tau_1 \to \infty} x_o(\tau_1) = 0 \tag{63}$$

And for $\eta < 0$

$$\begin{aligned} \lim_{\tau_1 \to \infty} x_o(\tau_1) = & \frac{x_o(0)}{|x_o(0)|} (\overline{\eta}/\delta)^{1/2} \\ = & \pm\sqrt{\overline{\eta}/\delta} \end{aligned} \tag{64}$$

where $\overline{\eta} = -\eta = D$.

In order to get more information let us consider the average of $x_0(\tau_1)^2$. To discuss $< x_0(\tau_1)^2 >$ we consider $x_0(\tau_1)$ as a stochastic variable and use the method which deals with the Fokker-Planck equation for $x_0(\tau_1)$ as in the previous work.[18]

When $\eta > 0$, from the deterministic type of equation for $< x_0(\tau_1)^2 >$ we obtain

$$<x_o(\tau_1)^2> \cong <x_o^2>_o \exp(-2\eta\tau_1) + \frac{\overline{D}}{\eta}[1 - \exp(-2\eta\tau_1)] \tag{65}$$

where $\overline{D}$ is the diffusion coefficient with respect to x_0.

If $\eta < 0$, we need to use the probability distribution function for $x_0(\tau_1)$ to get $< x_0(\tau_1)^2 >$. By using the approximate probability distribution obtained previously,[10,11,18] we get

$$<x_o^2>_{\tau_1} = (\bar{\eta}/\delta)[1 - \sqrt{\pi}\, Y \exp(Y^2) \operatorname{erfc}(Y)] \tag{66}$$

where

$$Y = [2\delta\sigma(\tau_1)/\bar{\eta}]^{-1/2} \tag{67}$$

with

$$\sigma(\tau_1) = \exp(2\bar{\eta}\tau_1) \tag{68}$$

and erfc(Y) is the complementary error function. For very long times, $<x_0^2>_{\tau_1}$ becomes

$$\begin{aligned} <x_o^2>_\infty = & \bar{\eta}/\delta \\ = & [x_o(\infty)]^2 \end{aligned} \tag{69}$$

Conclusion and Remarks

We have analyzed the nonlinear stability of the two Schlögl models in the presence of diffusion. The resulting equations (35) and (59) (or eq. (60)) for the amplitude of fluctuations show the stability behavior of the system. For $k^2 > k_c^2$, $x_0 = 0$ is the only stable solution. This means that the fluctuations vanish as time goes on, so the steady state $X_{st}^0 = 0$ is stable. Yet for $k^2 < k_c^2$, $x_0 = 0$ becomes unstable and evolves to the finite value as time goes to infinity. In other words, the fluctuation is enhanced and this reflects the fact that the system relaxes from unstable steady state to new stable steady state(s). The interesting result is that the critical behavior is caused by the diffusion effect. Without diffusion there occurs no critical point for our Schlögl models. Diffusion can be thought to play an important role in the dynamical behavior of the systems.

In k-space, the critical point k_c^2 is a bifurcation point across which new steady states emerge from a steady state. Since

k is proportional to the inverse of wavelength, the bifurcation toward new stable steady states occurs above the critical wavelength. This shows that a "long range order" is important in the formation of an ordered stable spatial pattern.

Several years ago, Matkowsky[16] presented a mathematical treatment of nonlinear dynamic stability problem. A partial differential equation of the same type as that discussed in this paper with a nonlinear source term is dealt with in his work. His main interest was to investigate the dependence of the solution on a certain parameter, which determines the stability property of the system, in the neighborhood of a critical (or bifurcation) point. So he derived a formal asymptotic representation for the solution in powers of a small parameter ε which is related to the nearness of the system from the critical point. Using the two time scaling method for nonlinear analysis, a recursive system of equations for each power of ε was obtained. From the orthogonality condition to be satisfied, he was able to get the first order nonlinear ordinary differential equation for the amplitude function. This amplitude function plays the same role of an order parametr as $x_0(\tau_1)$ in our analysis.

If we apply the Matkowsky's method to our models, the following result is obtained:

$$\frac{dA(\tau)}{d\tau} = -\xi A(\tau) - \sigma [A(\tau)]^3 \qquad (70)$$

for the amplitude function $A(\tau)$. Here σ is a positive constant which has a different value for each model and ξ has the value $+1$ in the stable region and -1 in the unstable region. This result is equivalent to ours. In principle, the two approaches are equivalent. Yet the Matkowsky's method can explain the effect of the type of initial perturbations. And it is easy to examine the dependence of the system's behavior on the form of rate expression using this approach. Therefore, it may be applied to more general cases.

But, since Matkowsky's work is more mathematical, we have some difficulties in getting physical meanings from the analysis. The procedure of constructing the evolution equation for the amplitude of fluctuations is more involved using his approach. And in his work the stability properties of the steady states are not easily found. In particular, if we deal with more complicated situations, *e.g.* reaction-diffusion systems with more than one intermediates, our approach would have advantages. An example of those systems is investigated in the previous work.[18].

Finally, it is noticed that in this analysis, the difference between quadratic and cubic models is not shown up clearly. They give the same type of equations for the amplitude of fluctuations in spite of the fact that they show different types of non-equilibrium transitions. Yet some authors[19] argued that for a quadratic nonlinearity, sufficiently close to the bifurcation point, the system was unable to show critical behavior. The similarities and differences of the two Schlögl models need more understanding. Types of nonlinearities will be more important if we deal with a system with more than one intermediates.

Acknowledgement. This work was supported by a grant from the Haksan Technical Research & Scholarship Foundation. Helpful discussions with Prof. D.J. Lee are also appreciated.

References

1. J. Ross, *Ber. Bunsenges. Physik. Chem.* **80**, 112 (1976).
2. J.R. Tucker and B.I. Halperin, *Phys. Rev.* **B3**, 3768 (1971).
3. M. Sargent, M.O. Scully, and W.E. Lamb, Jr., *Laser Physics* (Addison-Wesley, 1974).
4. F. Jhanig, *Biophys. J.*, **36**, 347 (1981).
5. E. Pytte and H. Thomas, *Phys. Rev.*, **179**, 431 (1969).
6. A. Nitzan, P. Ortoleva, J. Deutch, and J. Ross., *J. Chem. Phys.* **61**, 1056 (1974).
7. A. Nitzan, *Phys. Rev.* **A17**, 1513 (1978).
8. P.H. Richter, I. Procaccia, and J. Ross, *Adv. Chem. Phys.* **43**, 217 (1980).
9. D. Walgraef, G. Dewel, and P. Borckmans, *Adv. Chem. Phys.* **49**, 311 (1982).
10. K.H. Kim, K.J. Shin, D.J. Lee, and S.B. Ko, *Bull. Kor. Chem. Soc.* **6**, 295 (1985).
11. D.J. Lee, M.H. Ryu, and J.M. Lee, *Bull. Kor. Chem. Soc.* **6**, 91 (1985).
12. M. Suzuki, *Adv. Chem. Phys.* **46**, 195 (1981); and references therein.
13. K. Kawasaki and S.K. Kim, *J. Chem. Phys.* **68**, 319 (1978).
14. G. Nicolis and I. Prigogine, *Self-Organization in Non-equilibrium Systems* (Wiley, 1977).
15. A.M. Albano, N.B. Abraham, D.E. Chyba, and M. Martelli, *Am. J. Phys.* **52**, 161 (1984).
16. B.M. Matkowsky, *Bull. Am. Math. Soc.* **76**, 620 (1970).
17. S. Kogelman and J.B. Keller, SIAM *J. Appl. Math. Soc.* **20**, 619 (1971).
18. K.O. Han, D.J. Lee, J.M. Lee, K.J. Shin, and S.B. Ko, *Bull. Kor. Chem. Soc.* **7**, 224 (1986).
19. G. Nicolis and M. Malek-Mansour, *J. Stat. Phys.* **22**, 495 (1980).