

## References

- (1) A.A. Lamola, T. Yamane and A.M. Trozzolo, *Science*, **179** 1131 (1973).
- (2) H.U. Weltzine, *Biochim. Biophys. Acta*, **559** 259 (1979).
- (3) I.E. Kochevar, *J. Invest. Dermatol.*, **74** 256 (1980).
- (4) I.E. Kochevar and M. Yoon, *Photochem. Photobiol.*, **37** 279 (1983).
- (5) P. Walrant and R. Santus, *Photochem. Photobiol.*, **19** 411 (1974).
- (6) P. Walrant and R. Santus, *Photochem. Photobiol.*, **20** 455 (1974).
- (7) R. Yamauchi and S. Matsushida, *Agric. Biol. Chem.*, **41** 1425 (1977).
- (8) E. Amouyal, A. Bernas and D. Grand, *Photochem. Photobiol.*, **29** 1071 (1979).
- (9) F.G.r. Moses, R.S.H. Liu and B.M. Muroe, *Mol. Photochem.*, **1** 245 (1969).
- (10) E.P. Kirby and R.F. steiner, *J. Phys. Chem.*, **74** 4480 (1970).
- (11) K.A. Brown-Wensley, S.L. Mattes and S. Farid, *J. Am. Chem. Soc.*, **100** 4162 (1978).
- (12) J.R. Lakowicz, "Principles of Fluorescence Spectroscopy", pp 257, Plenum Press, N.Y. (1983).
- (13) C.R. Goldschmidt, R. Potashnik and M. Ottolenhi, *J. Phys. Chem.*, **75** 1025 (1971).
- (14) G.N. Taylor, *Chem. Phys. Lett.*, **10** 355 (1971).
- (15) C.S. Foote, "Singlet Oxygen" *Advances in Chemistry*, ACS, pp 139, Academic Press, N.Y. (1979).
- (16) J. Eriksen and C.S. Foote, *J. Am. Chem. Soc.*, **102** 6083 (1980).

## A Stochastic Investigation of a Dynamical System Exhibiting the Second-Order Phase Transition

Kyung Hee Kim and Kook Joe Shin†

*Department of Chemistry, Seoul National University, Seoul 151, Korea*

Dong Jae Lee\*

*Department of Chemistry, Chonbuk National University, Chonju, Chonbuk 520, Korea*

Seok Beom Ko

*Department of Chemical Education, Chonbuk National University, Chonju, Chonbuk 520, Korea*  
(Received June 11, 1985)

An approximate solution of the Fokker-Planck equation with the nonlinear drift term due to a Schlögl model is obtained and the result is compared with the methods proposed by Suzuki. Also the effect of nonlinearity on the correlation length at the stable steady state is studied.

## Introduction

In recent years, there have been considerable interests in the behavior of systems far from the thermodynamic equilibrium, which exhibits instability. Such phenomena are observed in many fields<sup>1-4</sup>. Especially, the laser model<sup>5</sup> draws a great attention. Recent investigations of several authors<sup>6, 7</sup> have provided the analogy between transitions in unstable systems and phase transitions. Their theory is applicable to any system whose macroscopic behavior is governed by nonlinear evolution equations.

If there is no random force which is caused by internal microscopic fluctuations, a system in an unstable state does not undergo decaying process. Once the decay of the unstable state is initiated, fluctuations are amplified by the linear contribution which shows exponential divergence. Later, these fluctuations are affected by the nonlinear effect and then have the

finite steady state value. This fact has been studied from the Langevin eq. by Suzuki<sup>8</sup> with his scaling theory and also by Valsakumar and his coworkers.<sup>9</sup>

Also several authors have tried to obtain the probability distribution function satisfying the Fokker-Planck equation. Among them, Suzuki<sup>8, 10</sup> has divided the whole range of time into three parts, that is, initial, intermediate and final regimes and introduced the scaling theory connecting the initial and intermediate regimes. This theory is successful in describing the intermediate regime but does not describe the final steady state properly. Later, he has proposed the unified theory<sup>11</sup> using the properties of the exponential streaming operator. In addition, Valsakumar<sup>12</sup> has obtained the formally exact probability distribution function using Trotter's formula, but it has a rather complicated form and is difficult to handle.

In this work we study a chemical system which can be described by a stochastic variable governed by a Fokker-Planck equation. The nonlinear drift term in the Fokker-Planck equation

†Present Address: Department of Applied Chemistry, National Fisheries University of Pusan, Pusan 608, Korea

is given by a Schlögl model which exhibits a second order phase transition. Recently, one of us reported the dynamic properties of a system near the stable steady state.<sup>15</sup> The model adopted there was another Schlögl model exhibiting the first order phase transition. Following their generalized version of Suzuki's scaling method of solution, we obtain in the first section an approximate solution of the Fokker-Planck equation with the present Schlögl model and also we get the second moment of the stochastic variable of the chemical system. In the next section, the time-dependent correlation length near the stable steady state is obtained by substituting the variable satisfying the rate expression into the equation which we treat. This method shows the effect of nonlinearity at the stable steady state.

### Theory

As an example of the system exhibiting the second order phase transition, let us consider a Schlögl model, which is given by

$$F[X(\vec{r}, t)] = \alpha X(\vec{r}, t) - \beta X(\vec{r}, t)^2 + \lambda(\vec{r}, t), \quad (1)$$

where  $\alpha$  and  $\beta$  are assumed to be positive constants,  $\lambda$  is a pumping parameter, and  $F[X]$  is the nonlinear rate expression. Another Schlögl model investigated earlier by one of us<sup>15</sup> contains a cubic term,  $-\beta X(\vec{r}, t)^3$ , instead of the above quadratic term and it belongs to a different category of stability which leads to the first order phase transition behavior. The present model exhibits a second order phase transition as discussed below.

This model describes the derivative of the concentration of the intermediate  $X$  with respect to time in the following chemical reaction scheme with concentrations of other species being held constant.



Steady states of eq. (1) are determined by the solution of the equation,  $F(X_{st}^0, \lambda_{st}^0) = 0$ . In Figure 1 we plot the curve  $Y = \alpha X_{st}^0 - \beta X_{st}^{02}$  as a function of  $X_{st}^0$ . If the value of  $Y$  becomes smaller than a certain transition value of  $Y = |\lambda_{st}^*|$ , we have two roots which correspond to two steady states. Since  $X_{st}^0$  is continuous at the transition point,  $|\lambda_{st}^*| = \alpha^2/4\beta$ , this model is regarded as showing the second order phase transition. The relationship between  $X_{st}^0$  and  $\lambda_{st}^0$  is shown better in Figure 2. From the linear stability theory it is well known that the steady state is on the stable branch if the first order derivative of  $\lambda_{st}^0$  with respect to  $X_{st}^0$  is positive and it is on the unstable branch if the derivative is negative. At the marginal stability point the derivative vanishes. For simplicity we let  $\lambda = 0$  in the Schlögl model. Then,  $X_{st}^0 = 0$  and  $X_{st}^0 = \alpha/\beta$  correspond to the unstable and the stable steady states, respectively.

Inhomogeneous nonlinear Langevin equation for the stochastic variable  $X(\vec{r}, t)$  is given as

$$\frac{\partial X(\vec{r}, t)}{\partial t} = D \nabla^2 X(\vec{r}, t) + F[X(\vec{r}, t)] + \eta(\vec{r}, t) \quad (3)$$

where  $D$  is the diffusion coefficient and  $\eta(\vec{r}, t)$  is a random force which satisfies the Gaussian condition.<sup>16</sup>

$$\begin{aligned} \langle \eta(\vec{r}, t) \rangle &= 0 \\ \langle \eta(\vec{r}, t) \eta(\vec{r}', t') \rangle &= -2D \delta(\vec{r} - \vec{r}') \delta(t - t') \end{aligned} \quad (4)$$

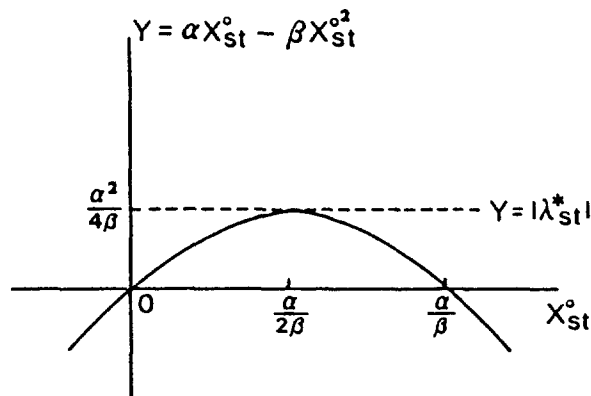


Figure 1. The quantity  $Y = \alpha X_{st}^0 - \beta X_{st}^{02}$  as a function of  $X_{st}^0$ .

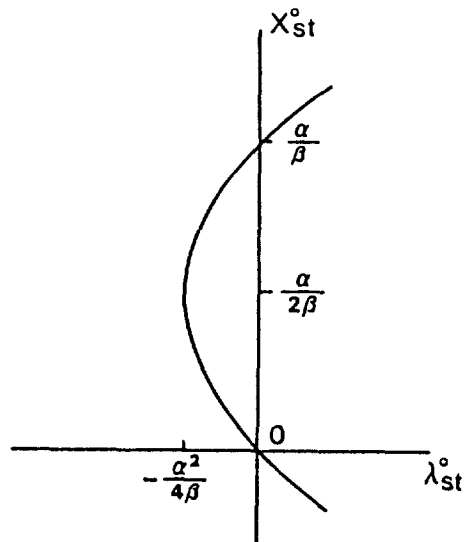


Figure 2. The dependence of  $X_{st}^0$  on  $\lambda_{st}^0$ .

Here,  $\delta(X)$  is the Dirac delta function. The equivalent Fokker-Planck equation to the above Langevin equation is

$$\begin{aligned} \frac{\partial}{\partial t} P(X, t) = & - \frac{\partial}{\partial X} \{ [D \nabla^2 X + F(X(\vec{r}, t))] P(X, t) \} + \\ & D \frac{\partial^2}{\partial X^2} P(X, t) \end{aligned} \quad (5)$$

#### (A) An approximate method to the solution of the nonlinear Fokker-Planck eq. with the Schlögl model.

Now let us consider the general Fokker-Planck eq. given by

$$\begin{aligned} \frac{\partial}{\partial t} P(X, t) = & - \frac{\partial}{\partial X} [F(X, t) P(X, t)] \\ & + \frac{\partial}{\partial X} \{ A(X, t) \frac{\partial}{\partial X} [A(X, t) P(X, t)] \} \end{aligned} \quad (6)$$

where  $A(X, t)$  and  $F(X, t)$  are the functions of  $X$  and  $t$ . This equation corresponds to the homogeneous Langevin equation, i.e., eq. (3) without the diffusion term.

We assume that the general solution  $P(X, t)$  has the following form

$$P(X, t) = N [b(t)/a(t)] H'(X, t) \exp[-\gamma(t) H(X, t)^2] \quad (7)$$

where  $N$  is the normalization constant,  $a(t)$ ,  $b(t)$  and  $\gamma(t)$  are functions of time, and  $H(X, t)$  is a functional of  $X$  and  $t$ . The prime in the expression  $H'(X, t)$  denotes the differentiation with respect to  $X$ . This form of the solution is a generalization of the scaling solution of Suzuki<sup>10</sup> in that his expression contains a functional of  $X$ ,  $f(X)$ , which appears in a similar fashion as in eq. (7) whereas our  $H(X, t)$  is a functional of both  $X$  and

t. The earlier work<sup>15</sup> by one of us also employed this assumption implicitly in the analysis of another Schlögl model. We substitute eq. (7) into eq. (6) and assume the following relations:

$$a(t) = A(X, t)H'(X, t). \tag{8a}$$

Then we obtain three relations:

$$\frac{\partial H(X, t)}{\partial t} = -[F(X, t) \frac{\partial H(X, t)}{\partial X}] \tag{8b}$$

$$-\frac{\partial \gamma(t)}{\partial t} = 4a(t)^2 \gamma(t)^2 \tag{8c}$$

$$\frac{\partial b(t)/\partial t}{b(t)} - \frac{\partial a(t)/\partial t}{a(t)} = -2a(t)^2 \gamma(t) \tag{8d}$$

From the above equations, we obtain the solution of eq. (6) in the following form

$$P(X, t) = \frac{H'(X, t)}{[\pi \{ \int_0^t a(\tau)^2 d\tau + c_1 \}]^{\frac{1}{2}}} \times \exp \left\{ -\frac{H(X, t)^2}{4 \left[ \int_0^t a(\tau)^2 d\tau + c_1 \right]} \right\} \tag{9}$$

where  $c_1 = 1/4\gamma(0)$ .

If we keep only the linear term in  $F(X, t)$  with  $A(X, t) = D^{1/2}$ , we get from eqs. (8b) and (8a).

$$a(t) = D^{\frac{1}{2}} \exp(-\alpha t), \tag{10}$$

For this linear case we obtain the following solution

$$P(X, t) = \left[ \frac{2}{\pi D} \frac{1}{e^{2\alpha t} - 1} \right]^{\frac{1}{2}} \cdot \exp \left\{ -\frac{(X - X_0 e^{\alpha t})^2}{2 \left[ \frac{D}{\alpha} (e^{2\alpha t} - 1) \right]} \right\}, \tag{11}$$

where we let  $c_1 = 0$  for simplicity.

This is the well-known Ornstein-Uhlenbeck solution.<sup>13</sup> Therefore, it might be a reasonable approximation to choose  $a(t) = D^{1/2}e^{-\alpha t}$  for the nonlinear case. The resulting nonlinear probability distribution,  $P(X, t)$ , is given by

$$P(X, t) = \left[ \frac{2}{\pi D(t)} \right]^{\frac{1}{2}} \cdot G'(X, t) \cdot \exp \left\{ -\frac{G(X, t)^2}{2D(t)} \right\} \tag{12}$$

where in our model

$$D(t) = \frac{D}{\alpha} (e^{2\alpha t} - 1) \tag{12a}$$

$$H(X, t) = X e^{-\alpha t} \left[ 1 - \frac{\beta}{\alpha} X (1 - e^{-\alpha t}) \right]^{-1} \tag{12b}$$

$$G(X, t) \equiv e^{\alpha t} H(X, t) = X \left[ 1 - \frac{\beta}{\alpha} X (1 - e^{-\alpha t}) \right]^{-1} \tag{12c}$$

and the prime in the expression  $G'(X, t)$  denotes the differentiation with respect to  $X$ . As time goes to infinity, this probability distribution becomes Suzuki's scaling solution<sup>10</sup> in the following form:

$$P_{sc}(X, t) = \left[ \frac{2}{\pi D(t)} \right]^{\frac{1}{2}} \cdot G'(X) \cdot \exp \left\{ -\frac{G(X)^2}{2D(t)} \right\} \tag{13}$$

where

$$D(t) = \frac{D}{\alpha} e^{2\alpha t} \tag{13a}$$

$$G(X) = X \left[ 1 - \frac{\beta}{\alpha} X \right]^{-1} \tag{13b}$$

At the stable steady state, the probability distribution is given by

$$P(X_{st}) = A \exp \left\{ -\frac{\beta}{3D} X_{st}^3 + \frac{\alpha}{2D} X_{st}^2 \right\} \tag{14}$$

where  $A$  is a normalization constant. The time evolution of the probability distribution is shown in Figure 3.

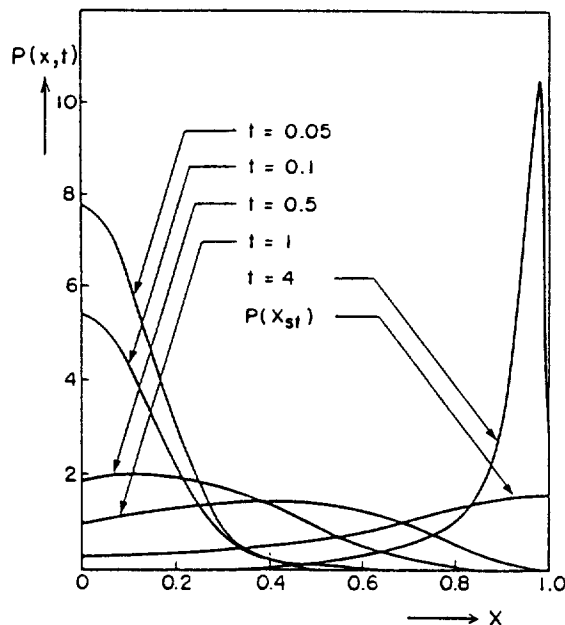


Figure 3. The dependence of  $P(X, t)$  on time. ( $\alpha = \beta = 1, D = 0.1$ ).

If the diffusion term is included in the rate expression, the probability distribution may be obtained in the long time and weakly nonlinear regime according to the method of Kawasaki and Kim.<sup>17</sup>

The average of  $X(t)^2$  depending on time is

$$\langle X(t)^2 \rangle = \int_0^\infty dX X^2 P(X, t) / \int_0^\infty dX P(X, t) \tag{15}$$

Using eq. (12), we have

$$\langle X(t)^2 \rangle = \left[ \frac{2}{\pi D(t)} \right]^{\frac{1}{2}} \int_0^\infty \left[ \frac{G}{1 + \frac{\beta}{\alpha} (1 - e^{-\alpha t}) G} \right]^2 \times \exp \left[ -\frac{G^2}{2D(t)} \right] dG \tag{16}$$

Explicit calculations are given in Appendix. As time goes to infinity, its limiting value is  $(\alpha/\beta)^2$ , i.e.,

$$\lim_{t \rightarrow \infty} \langle X(t)^2 \rangle = \left( \frac{\alpha}{\beta} \right)^2 \tag{17}$$

The average value of  $X_{st}^2$  at the stable steady state is given by

$$\langle X_{st}^2 \rangle = \int_0^\infty dX_{st} X_{st}^2 P(X_{st}) / \int_0^\infty dX_{st} P(X_{st}). \tag{18}$$

For arbitrary  $\alpha$  and  $\beta$ , we can obtain this value by the numerical integration using Simpson's formula and we found that

$$\langle X_{st}^2 \rangle = \lim_{t \rightarrow \infty} \langle X(t)^2 \rangle. \tag{19}$$

**(B) Time correlation functions for the fluctuating variables.**

In this section, we shall discuss the time correlation functions at a stable steady state when the system relaxes from an unstable state.

In order to consider the effect of the random force on the variable, let us separate the variable into two parts, that is, the variable  $X^0(\vec{r}, t)$  governed by the rate expression and a fluctuating part due to the random force,  $dX(\vec{r}, t)$ .

Then we obtain

$$\frac{\partial}{\partial t} X^0(\vec{r}, t) = D \nabla^2 X^0(\vec{r}, t) + \alpha X^0(\vec{r}, t) - \beta X^0(\vec{r}, t)^2 \tag{20a}$$

$$\frac{\partial}{\partial t} \delta X(\vec{r}, t) = D \nabla^2 \delta X(\vec{r}, t) + [\alpha - 2\beta X^*(\vec{r}, t)] \delta X(\vec{r}, t) - \beta \delta X(\vec{r}, t)^2 + \eta(\vec{r}, t). \quad (20b)$$

Eq. (20b) can be written as

$$\frac{\partial}{\partial t} \delta X(\vec{k}, t) = -[Dk^2 + 2\beta X^*(t) - \alpha] \delta X(\vec{k}, t) + \eta(\vec{k}, t) - \frac{\beta}{(2\pi)^6} \int d\vec{k}_1 d\vec{k}_2 \delta(\vec{k} - \vec{k}_1 - \vec{k}_2) \delta X(\vec{k}_1, t) \delta X(\vec{k}_2, t) \quad (21)$$

by introducing the Fourier transform as follows:

$$f(\vec{k}, t) = \int d\vec{r} e^{-i\vec{k} \cdot \vec{r}} f(\vec{r}, t) \quad (22a)$$

$$f(\vec{r}, t) = \frac{1}{(2\pi)^3} \int d\vec{k} e^{i\vec{k} \cdot \vec{r}} f(\vec{k}, t). \quad (22b)$$

The solution of eq. (20a) can be written as

$$X^*(t) = X^*(O) e^{\alpha t} [1 - \frac{\beta}{\alpha} X^*(O) (1 - e^{\alpha t})]^{-1} \quad (23)$$

Here we assume the following Gaussian condition

$$\langle \delta X(\vec{k}, O) \eta(\vec{k}, t) \rangle = 0 \quad (24)$$

$$\langle \delta X(\vec{k}, t_1) \delta X(\vec{k}, t_2) \cdots \delta X(\vec{k}, t_n) \rangle = 0 \text{ if } n \text{ is an odd integer, sum over all the possible pair products if } n \text{ is an even integer.}$$

Now we define a time correlation function as

$$G(\vec{k}, t, t') = \langle \delta X(\vec{k}, t) \delta X(\vec{k}', t') \rangle \delta(\vec{k} - \vec{k}'). \quad (25)$$

We first consider eq. (21) neglecting the nonlinear term. Using the condition, eq. (24), the time correlation function is given by

$$G^*(\vec{k}, t) = \langle \delta X(\vec{k}, O)^2 \rangle \cdot \exp \left\{ -D \int_0^t (k^2 + \frac{2\beta X^*(t') - \alpha}{D}) dt' \right\} \quad (26)$$

At a stable steady state the correlation function is

$$G^*(\vec{k}, t) = \langle \delta X(\vec{k}, O)^2 \rangle \exp \{-D(k^2 + \xi^{-2})t\} \quad (27)$$

where  $\xi$  is the time-independent correlation length defined as

$$\xi^{-2} = \frac{1}{D} (2\beta X_{st}^* - \alpha) = \frac{\alpha}{D} \quad (28)$$

If we consider the time-dependent  $X^*(t)$  given by eq. (23), the time-dependent correlation function is

$$G^*(\vec{k}, t) = \langle \delta X(\vec{k}, O)^2 \rangle \cdot \exp \{-D[k^2 + \xi(t)^{-2}]t\} \quad (29)$$

where the time-dependent correlation length,  $\xi(t)$ , is defined as

$$\xi(t)^{-2} = \frac{2}{Dt} \ln \left\{ 1 - \frac{\beta}{\alpha} X(O) (1 - e^{\alpha t}) \right\} - \frac{\alpha}{D} \quad (30)$$

As time goes to infinity, the time-dependent correlation length is equal to the time-independent correlation length. Next, we consider the effect of nonlinearity on the correlation function. Using the condition, eq. (24), the time correlation function is derived in the following way:

Multiplying eq. (21) by  $\delta X(\vec{k}, O)$  and averaging it, we obtain

$$\begin{aligned} \frac{\partial}{\partial t} \langle \delta X(\vec{k}, t) \delta X(\vec{k}, O) \rangle &= -[Dk^2 + 2\beta X^*(t) - \alpha] \\ &\times \langle \delta X(\vec{k}, t) \delta X(\vec{k}, O) \rangle - \frac{\beta}{(2\pi)^6} \int d\vec{k}_1 d\vec{k}_2 \delta(\vec{k} - \vec{k}_1 - \vec{k}_2) \\ &\times \langle \delta X(\vec{k}_1, t) \delta X(\vec{k}_2, t) \delta X(\vec{k}, O) \rangle \end{aligned} \quad (31)$$

If  $X^*(t)$  has the steady state value, the solution of eq. (21) is given by

$$\delta X(\vec{k}, t) = \delta X(\vec{k}, O) \exp[-D(k^2 + \xi^{-2})t]$$

$$\begin{aligned} &+ \int_0^t \eta(\vec{k}, t') \exp[-D(k^2 + \xi^{-2})(t - t')] dt' \\ &- \frac{\beta}{(2\pi)^6} \int_0^t dt' \exp[-D(k^2 + \xi^{-2})(t - t')] \\ &\times \int d\vec{k}_1 d\vec{k}_2 \delta(\vec{k} - \vec{k}_1 - \vec{k}_2) \delta X(\vec{k}_1, t') \delta X(\vec{k}_2, t') \\ &\equiv \delta X_0(\vec{k}, t) + \delta X_1(\vec{k}, t) \end{aligned} \quad (32)$$

where each term is defined as

$$\begin{aligned} \delta X_0(\vec{k}, t) &= \delta X(\vec{k}, O) \exp[-D(k^2 + \xi^{-2})t] \\ &+ \int_0^t \eta(\vec{k}, t') \exp[-D(k^2 + \xi^{-2})(t - t')] dt' \end{aligned} \quad (32a)$$

$$\begin{aligned} \delta X_1(\vec{k}, t) &= -\frac{\beta}{(2\pi)^6} \int_0^t dt' \exp[-D(k^2 + \xi^{-2})(t - t')] \\ &\times \int d\vec{k}_1 d\vec{k}_2 \delta(\vec{k} - \vec{k}_1 - \vec{k}_2) \delta X(\vec{k}_1, t') \delta X(\vec{k}_2, t') \end{aligned} \quad (32b)$$

From eq. (31) the time correlation function is given by

$$G(\vec{k}, t) = \langle \delta X(\vec{k}, O)^2 \rangle \exp \{-D[k^2 + \xi_r^{-2}(t)]t\} \quad (33)$$

where the correlation length with the nonlinear effect,  $\xi_r(t)$ , is defined as

$$\xi_r^{-2}(t) = \xi^{-2} + \frac{\beta}{32\pi^6 D} \langle \delta X_1(O, t) \rangle \quad (34)$$

with  $\xi$  given by eq. (28). As time goes to infinity, the value of  $\langle \delta X_1(O, t) \rangle$  becomes finite. That is,

$$\lim_{t \rightarrow \infty} \langle \delta X_1(O, t) \rangle = -\frac{\beta D}{\alpha^2 (2\pi)^6}. \quad (35)$$

Therefore, the above correlation length in the long time limit is given by

$$\lim_{t \rightarrow \infty} \xi_r^{-2}(t) = \xi^{-2} - \frac{2\beta^2}{\alpha^2 (2\pi)^{12}} \quad (36)$$

As shown in the above result, the correlation length with the nonlinear effect is larger than the correlation length obtained with the linear approximation.

If we consider the time dependence of  $X^*(t)$ , the solution of eq. (21) is given by

$$\begin{aligned} \delta X(\vec{k}, t) &= \delta X(\vec{k}, O) \exp \left\{ -\int_0^t [Dk^2 + 2\beta X^*(t') - \alpha] dt' \right\} \\ &+ \int_0^t \eta(\vec{k}, t') \exp \left\{ -\int_{t'}^t [Dk^2 + 2\beta X^*(t'') - \alpha] dt'' \right\} dt' \\ &- \frac{\beta}{(2\pi)^6} \int_0^t dt' \exp \left\{ -\int_{t'}^t [Dk^2 + 2\beta X^*(t'') - \alpha] dt'' \right\} \\ &\times \int d\vec{k}_1 d\vec{k}_2 \delta(\vec{k} - \vec{k}_1 - \vec{k}_2) \delta X(\vec{k}_1, t') \delta X(\vec{k}_2, t') \\ &\equiv \delta X'_0(\vec{k}, t) + \delta X'_1(\vec{k}, t) \end{aligned} \quad (37)$$

where each term is defined similarly as in eq. (32). From eq. (31) the corresponding correlation function is given by

$$G(\vec{k}, t) = \langle \delta X(\vec{k}, O)^2 \rangle \exp \{-D[k^2 + \xi_r^{-2}(t)]t\} \quad (38)$$

where the correlation length,  $\xi_r(t)$ , with the nonlinear effect and the general time-dependent  $X^*(t)$  is defined as

$$\xi_r^{-2}(t) = \xi^{-2}(t) + \frac{2\beta}{D(2\pi)^6} \langle \delta X'_1(O, t) \rangle \quad (39)$$

with  $\xi(t)$  given by eq. (30). Near the stable steady state the contribution of  $\langle \delta X'_1(O, t) \rangle$  to the correlation length is finite;

$$\lim_{t \rightarrow \infty} \langle \delta X'_1(O, t) \rangle = -\frac{\beta D}{\alpha^2 (2\pi)^6} \quad (40)$$

So, the above correlation length near the stable steady state is given by

$$\xi_{R^{-2}}(t) = \xi^{-2}(t) - \frac{2\beta^2}{\alpha^2(2\pi)^{1/2}} \quad (41)$$

and at the stable steady state this correlation length is equal to  $\xi_R(t)$ .

## Discussion

In the first part of this work we have obtained an approximate solution  $P(X, t)$  to the Fokker-Planck equation with the nonlinear drift term due to a Schlögl model in terms of the function  $G(X, t)$  which is a functional of  $X$  and  $t$ . This solution may be compared with the recently proposed Suzuki's solution. That is, the solution obtained after the first-order decoupling of the exponential operator in Suzuki's unified theory<sup>11</sup> is exactly equal to ours. This distribution function  $P(X, t)$  does not describe the approach to the final stable steady state properly. The reason why the present probability distribution function does not approach to the final steady state distribution function given by eq. (14) is that our approximate method of solution is based on the scaling theory of Suzuki. At present no exact solution to the nonlinear Fokker-Planck equation is available and the best approximate solution to date is based on the scaling theory or at best some modification of it. Since the scaling theory is dealing with the initial and intermediate regimes and the description of the passage to the final regime is only at the formal and still approximate level.<sup>11, 12</sup> However, the second moment approaches the final steady state value in the long time limit. Some attempts have been made to resolve this problem but it seems rather difficult and more vigorous study is needed.

Secondly, we have obtained several correlation lengths at the stable steady state and we conclude that the correlation length with the effect of nonlinearity is larger than the correlation length considering the linear term only.

## Appendix

We obtained eq. (16) with the following form

$$\begin{aligned} \langle X(t)^2 \rangle &= \left[ \frac{2}{\pi D(t)} \right]^{1/2} \int_0^\infty \left[ \frac{G}{1 + \frac{\beta}{\alpha}(1 - e^{-\alpha t})G} \right]^2 \\ &\quad \times \exp\left[-\frac{G^2}{2D(t)}\right] dG. \end{aligned} \quad (A1)$$

Transforming  $G^2/D(t)$  into  $u^2$ , we have

$$\langle X(t)^2 \rangle = \sqrt{\frac{2}{\pi}} \cdot D(t) \int_0^\infty \left( \frac{u}{1+Bu} \right)^2 \cdot \exp\left(-\frac{u^2}{2}\right) du \quad (A2)$$

where

$$B = \frac{\beta}{\alpha} D(t)^{1/2} (1 - e^{-\alpha t}).$$

In the above eq. (A2) the integrated part is divided into two parts.

$$\begin{aligned} \int_0^\infty \left( \frac{u}{1+Bu} \right)^2 \cdot \exp\left[-\frac{u^2}{2}\right] du &= \frac{1}{B^2} \int_0^\infty e^{-u^2/2} du - \left( \frac{1}{B^2} - \frac{1}{B} \frac{d}{dB} \right) \\ &\quad \times \left\{ \int_0^\infty \frac{1}{1+Bu} \cdot e^{-\frac{u^2}{2}} du \right\} \end{aligned} \quad (A3)$$

The first term on the rhs is easily integrable and the second term is given by<sup>14</sup>.

$$\int_0^\infty \frac{1}{1+Bu} \cdot e^{-\frac{u^2}{2}} du = \frac{1}{B} e^{-\frac{1}{2B^2}} \left\{ \sqrt{\pi} \int_0^{\frac{1}{\sqrt{2B}}} e^{t^2} dt - \frac{1}{2} E_i\left(\frac{1}{2B^2}\right) \right\} \quad (A4)$$

where  $E_i(X)$  is the exponential integral function which is defined as<sup>14</sup>

$$E_i(X) = \gamma + \ln X + \sum_{n=1}^\infty \frac{X^n}{n \cdot n!} \quad (X > 0, \gamma = 0.5771). \quad (A5)$$

Using the above definition, eq. (A2) can be written as

$$\begin{aligned} \langle X(t)^2 \rangle &= \frac{1}{A^2} - \frac{\sqrt{2}}{\pi} \frac{1}{A^2 B} \cdot e^{-\frac{1}{2B^2}} \left\{ \sqrt{\pi} \int_0^{\frac{1}{\sqrt{2B}}} e^{t^2} dt - \frac{1}{2} E_i\left(\frac{1}{2B^2}\right) \right\} \\ &\quad + \frac{\sqrt{2}}{\pi} \cdot \left( \frac{1}{A^2 B^3} - \frac{1}{A^2 B} \right) \cdot e^{-\frac{1}{2B^2}} \left\{ \sqrt{\pi} \int_0^{\frac{1}{\sqrt{2B}}} e^{t^2} dt - \frac{1}{2} E_i\left(\frac{1}{2B^2}\right) \right\} \\ &\quad - \frac{\sqrt{\pi}}{2} \cdot \frac{1}{A^2 B^2} + \frac{1}{A^2 B} \cdot e^{-\frac{1}{2B^2}} \left\{ 1 + \sum_{n=1}^\infty \frac{1}{n!} \left(\frac{1}{2B^2}\right)^n \right\} \end{aligned} \quad (A6)$$

where

$$A = \frac{\beta}{\alpha} (1 - e^{-\alpha t}).$$

As time goes to infinity,  $B$  also goes to infinity and only the first term on the rhs of eq. (A6) survives.

From this fact we can have

$$\lim_{t \rightarrow \infty} \langle X(t)^2 \rangle \simeq \frac{1}{A^2} \simeq \left( \frac{\alpha}{\beta} \right)^2. \quad (A7)$$

**Acknowledgement.** This work is supported by a grant from the Basic Science Research Institute Program, Ministry of Education, Republic of Korea.

## 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) F. Jhanig, *Biophys. J.*, **36**, 347 (1981).
- (4) E. Pytte and H. Thomas, *Phys. Rev.*, **179**, 431 (1969).
- (5) M. Sargent, M.O. Scally, and W.E. Lamb, Jr., "Laser Physics" (Addison-Wesley, 1974).
- (6) F. Schlögl, *Z. Physik*, **253**, 147 (1972).
- (7) A. Nitzan, P. Ortholeva, J. Deutch, and J. Ross, *J. Chem. Phys.*, **61**, 1058 (1974).
- (8) M. Suzuki, *Adv. Chem. Phys.*, **46**, 195 (1981).
- (9) M.C. Valsakumar, K.P.N. Murthy, and G. Ananthakrishna *J. Stat. Phys.*, **30**, 617 (1983).
- (10) M. Suzuki, *Prog. Theor. Phys.*, **56**, 77 (1976); *J. Stat. Phys.*, **16**, 11 (1977).
- (11) M. Suzuki, *Physica*, **117A**, 103 (1983).
- (12) M.C. Valsakumar, *J. Stat. Phys.*, **32**, 545 (1983).
- (13) G.E. Uhlenbeck and L. S. Ornstein, *Phys. Rev.*, **36**, 823 (1930).
- (14) M. Abramowitz and I.A. Stegun, "Handbook of Mathematical Functions" (Dover, 1964).
- (15) D.J. Lee, M.H. Yoo, and J.M. Lee, *Bull. Korean Chem. Soc.* **6**, 91 (1985).
- (16) "Selected Papers on Noise and Stochastic Processes", ed. N. Wax (Dover, 1954).
- (17) K. Kawasaki and S.K. Kim, *J. Chem. Phys.* **68**, 319 (1978).