

# The Time Correlation Function Near (and at) a Stable Steady State, When a Chemical System Relaxes from the Unstable Steady State\*

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The dynamic properties near (and at) a stable steady state are discussed, when a chemical system relaxes from the unstable steady state. The time-dependent correlation length for the fluctuating variable near a stable steady state is explicitly obtained by introducing the probability average for the variable satisfying the rate equation. The study is carried out about the effect of nonlinearity on the correlation length near (and at) a stable steady state.

## 1. Introduction

In recent years major efforts in statistical theory have been directed to the phenomena far from equilibrium (or steady state), which exhibit instability. Such phenomena are very frequently observed in many kinds of experiments, such as chemical reaction,<sup>1</sup> laser<sup>2</sup>, superconductor<sup>3</sup>, biological system<sup>4</sup> and *etc.*<sup>5</sup> The study of these phenomena reduces to the stability of solutions of the phenomenological equations of motion. One of the most interesting phenomena related to the instability is the relaxation and transition from an unstable state to a stable state. Suzuki<sup>6</sup> is one of the pioneers to investigate such phenomena theoretically. In order to study the relaxation from an instability point to the equilibrium state he has introduced a time scaling theory that the whole range of time is divided into three regimes, *i.e.*, the initial region in which the linear approximation is valid, the scaling regime in which the fluctuation enhancement occurs, and the final regime in which the system approaches the equilibrium state. In the scaling regime he has shown that the nonlinear terms in the stochastic equation can be treated as a singular perturbation. Kawasaki and his coworkers<sup>7</sup> have presented a dynamic theory for the enhanced fluctuations in a time-dependent Ginzburg-Landau (TDGL) model with the order parameter not conserved which is quenched from a thermodynamically stable state to an unstable state. They have shown that in a certain weak coupling, long time and long distance limit, diffusion and saturation effects can be treated separately. Kawasaki and Kim<sup>8</sup> have extended the theory to the chemical instability with diffusion, taking the Schlögl models as examples.

The purpose of the present paper is to study the time correlation function for the fluctuating variables due to the random force in a chemical system with instability near (and at) a stable steady state, when the system relaxes from an unstable steady state. The correlation function near a steady state is usually obtained by the conventional method, that is, linearization of a nonlinear Langevin equation or Fokker-Planck equation around the steady state.<sup>9</sup> Binder<sup>10</sup> has defined a time-dependent

correlation length by using the time average method for the variable, which obeys the macroscopic equation of motion, to discuss the spatial fluctuations in TDGL. In this paper we study a Schlögl model with two stable steady states and one unstable steady state. The time-dependent correlation length near a stable steady state in the model may not be obtained by using the conventional method or time average method, when the system relaxes from the unstable steady state to a stable steady state. Thus, we introduce the probability average for the variable satisfying the rate equation. The introduction of the probability average method enables us to calculate the time-dependent correlation length near a stable steady state. This method shows how the time-dependent correlation length is different from the time-independent correlation length at a stable steady state. The effect of nonlinearity on the correlation length is investigated by using a renormalization method. The present work is certainly valid in the region not close to the marginal stability state or critical point, where the more study may be required.

The procedure of the present paper is as follows; Starting from the nonlinear Langevin equation, we separate the variable into two parts, that is, a macroscopic part which satisfies the rate equation and the fluctuating part due to the random force. At first, we discuss the statistical properties of the macroscopic variable by using the proper probability distribution. Then, instead of the conventional definition for the correlation length, we use the probability average for the macroscopic variable, which enables us to calculate the time-dependent correlation length near a stable steady state explicitly. Finally, we obtain the renormalized correlation length near (and at) a stable steady state.

## 2. Theory

Let us consider a chemical system composed of a set of chemical species. If the concentration  $X(\vec{r}, t)$  of reacting species at position  $\vec{r}$  and time  $t$  satisfies a Langevin equation, an inhomogeneous nonlinear Langevin equation is described as

$$\frac{\partial}{\partial t} X(\vec{r}, t) = D \nabla^2 X(\vec{r}, t) + F[X(\vec{r}, t)] + \eta(\vec{r}, t), \quad (2.1)$$

where  $D$  is the diffusion coefficient,  $F$  the rate expression and  $\eta(\vec{r}, t)$  a random force which satisfies the Gaussian condition

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$$\langle \eta(\vec{r}, t) \rangle = 0, \quad \langle \eta(\vec{r}, t) \eta(\vec{r}', t') \rangle = 2D\delta(t-t'). \quad (2.2)$$

Here,  $\delta(x)$  is the Dirac delta function.

The equivalent Fokker-Planck equation to the above Langevin equation is

$$\frac{\partial}{\partial t} P(X, t) = -\frac{\partial}{\partial X} [D\nabla^2 X + F(X, t)]P(X, t) + D\frac{\partial^2}{\partial X^2} P(X, t). \quad (2.3)$$

The rate expression under consideration is the Schlögl model<sup>8</sup>, which shows two stable steady branches and one unstable branch, given by

$$F(X) = \alpha X - \beta X^3 + \lambda, \quad (2.4)$$

where  $\alpha$  and  $\beta$  are assumed to be positive constants and  $\lambda$  a pump parameter.

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  $X^\circ$  governed by the rate expression and a fluctuating part due to the random force,

$x(\vec{r}, t)$ . Then, we may write eq. (2.1) by

$$\begin{aligned} \frac{\partial}{\partial t} X^\circ(\vec{r}, t) &= D\nabla^2 X^\circ(\vec{r}, t) + \alpha X^\circ(\vec{r}, t) \\ &\quad - \beta X^\circ(\vec{r}, t)^3 + \lambda^\circ(\vec{r}, t), \end{aligned} \quad (2.5a)$$

$$\begin{aligned} \frac{\partial}{\partial t} x(\vec{r}, t) &= [D\nabla^2 + \alpha - 3\beta X^\circ(\vec{r}, t)^2] x(\vec{r}, t) - 3\beta X^\circ(\vec{r}, t) \\ &\quad x(\vec{r}, t)^2 - \beta x(\vec{r}, t)^3 + \delta\lambda(\vec{r}, t) + \eta(\vec{r}, t). \end{aligned} \quad (2.5b)$$

where  $\lambda^\circ$  is the pumping parameter governed by the rate expression and  $\delta\lambda$  the fluctuating part due to the random force.

In the following section we shall at first discuss statistical properties for the variable  $X^\circ$  and then shall discuss the correlation function between the fluctuating variables.

**The Statistical Properties for the Variable Governed by Rate Equation.** The following equation is given at a homogeneous steady state.

$$\lambda_s = -\alpha X_s^\circ + \beta X_s^{\circ 3} \quad (2.6)$$

where  $X_s^\circ$  denotes the value of a steady state. When the first order derivative of  $\lambda_s$  with respect to  $X_s^\circ$  is positive, the steady state is stable. If  $d\lambda_s/dX_s^\circ < 0$ , the steady state is unstable. At a marginal stability point, the first order derivative of  $\lambda_s$  with respect to  $X_s^\circ$  vanishes, while the second order derivative is nonzero. The point, which shows  $d\lambda_s/dX_s^\circ = 0$  and  $d^2\lambda_s/d^2X_s^\circ = 0$  corresponds to the critical point. The above properties are expressed in Figure 1. The detailed discussion has been given in ref. 9. From now on we consider only the case of  $\lambda = 0$ . The unstable steady state corresponds to  $X_s^\circ = 0$ , while the stable steady states are  $X_s^\circ = \pm(\alpha/\beta)^{1/2}$ .

In order to understand the relaxation from the unstable steady state to a stable steady state, let us substitute the homogeneous Schlögl model in the Fokker-Planck equation and then the moment of  $2n$  order ( $n$  is a positive number) satisfies the following equation of hierarchy

$$\frac{d}{dt} \langle X^{\circ 2n} \rangle = 2n(2n-1)D \langle X^{\circ 2n-2} \rangle + 2n[\alpha \langle X^{\circ 2n} \rangle$$

$$- \beta \langle X^{\circ 2n+2} \rangle].$$

The fluctuation  $\langle X^{\circ 2} \rangle$  at time  $t$  is obtained by neglecting the higher order moment

$$\langle X^{\circ 2} \rangle = (D/\alpha) (\exp(2\alpha t) - 1).$$

As time goes to infinity,  $\langle X^{\circ 2} \rangle$ , becomes divergent. This divergence comes from neglecting the nonlinear term. This shows that the nonlinear term cannot be neglected when the relaxation from the unstable to a stable steady state is discussed. Thus, we need to solve the equation of hierarchy. Actually, Shimizu<sup>11</sup> has used a system-size expansion method to study the relaxation from the unstable steady state. Instead of solving the equation of hierarchy the more efficient method is to obtain the proper probability distribution. Suzuki<sup>6</sup> has proposed a time scaling theory to obtain the probability distribution after long time. Extending Suzuki's probability distribution slightly without using the scaling method, we may obtain the probability distribution as<sup>7,12</sup>

$$P(X^\circ, t) = \frac{G(X^\circ, t)'}{[\pi D(t)]^{1/2}} \exp\left[-\frac{G(X^\circ, t)^2}{2D(t)}\right], \quad (2.7)$$

where the prime denotes differentiation with respect to  $X^\circ$  and  $G(X^\circ, t)$  and  $D(t)$  are given as

$$\begin{aligned} \frac{\partial}{\partial t} G(X^\circ, t) &= -F\frac{\partial}{\partial X^\circ} G(X^\circ, t), \\ D(t) &= (D/\alpha) [\exp(2\alpha t) - 1]. \end{aligned} \quad (2.8)$$

Taking the Schlögl model given in eq. (2.4),  $G(X^\circ, t)$  becomes

$$\begin{aligned} G(X^\circ, t) &= \exp(\alpha t) H(X^\circ, t) \\ H(X^\circ, t) &= X^\circ \exp(-\alpha t) [1 - X^{\circ 2}(\beta/\alpha)(1 - \exp(-2\alpha t))]^{-1/2}. \end{aligned} \quad (2.9)$$

$$X^\circ(t) = X^\circ(0) \exp(\alpha t) [1 - X^{\circ 2}(0)^2(\beta/\alpha)(1 - \exp(2\alpha t))]^{-1/2}.$$

At the initial unstable steady state the distribution becomes the delta distribution. For short time  $P(X^\circ, t)$  reduces to the Gaussian distribution given as

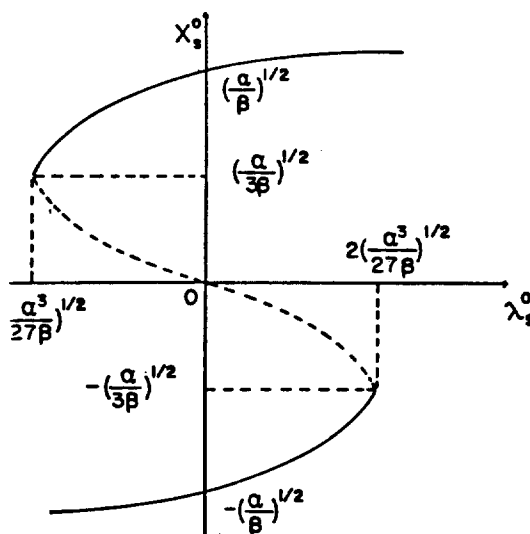


Figure 1. Dependence of  $X_s^\circ$  on  $\lambda_s^\circ$  on  $\lambda_s^\circ$ .

$$P(X^\circ, t) = \frac{1}{[2\pi Dt]^{1/2}} \exp\left(-\frac{X^{\circ 2}}{4Dt}\right).$$

After long time the distribution becomes the Suzuki probability distribution<sup>6,7</sup>

$$P(X^\circ, t) = \frac{G(X^\circ)'}{[\pi D(t)]^{1/2}} \exp\left[-\frac{G(X^\circ)^2}{2D(t)}\right], \quad (2.10)$$

where

$$\begin{aligned} G(X^\circ) &= X^\circ (1 - X^{\circ 2} (\beta/\alpha))^{-1/2}, \\ D(t) &= (D/\alpha) \exp(2\alpha t). \end{aligned} \quad (2.11)$$

As time goes to infinity, the system will finally reach a stable steady state, where the probability distribution may be expressed as<sup>12</sup>

$$\begin{aligned} P(X_s^\circ) &= -i \left(\frac{2\beta}{\alpha}\right)^{1/2} \exp\left(\frac{\alpha^2}{8D\beta}\right) K_{1/4}\left(\frac{\alpha^2}{8D\beta} \exp(2\pi i)\right)^{-1} \\ &\quad \exp\left[-\frac{\beta}{4D} \left(X_s^{\circ 2} - \frac{\alpha}{\beta}\right)^2\right], \end{aligned} \quad (2.12)$$

where  $i = \sqrt{-1}$  and  $K_{1/4}(x)$  is the Bessel function of imaginary argument of order  $1/4$ . The dependence of the probability distribution on time is shown in Figure 2.

Now, let us consider the rate equation with diffusion coefficient. Kawasaki and Kim<sup>8</sup> have presented a theory by which the solution of a class of nonlinear rate equations describing chemical reactions with instability and diffusion are related to the solutions of the same questions without diffusion in a certain long time and weakly nonlinear regime. Using their method, the probability distribution may be obtained, replacing  $\alpha$  in  $G(X^\circ)$  and  $D(t)$  by  $D\nabla^2 + \alpha$ . Thus, in the present paper we consider only the homogeneous case.

The average of  $X_s^{\circ 2}$ , using eq. (2.12), is

$$\langle X_s^{\circ 2} \rangle = \int_{-\infty}^{\infty} dX_s^\circ X_s^{\circ 2} P(X_s^\circ) = \frac{\alpha}{2\beta} \left[1 - \frac{K_{3/4}\left(\frac{\alpha^2}{8D\beta}\right)}{K_{1/4}\left(\frac{\alpha^2}{8D\beta}\right)}\right]. \quad (2.13)$$

In the case of  $\alpha^2/D\beta \gg 1$ , we have

$$\langle X_s^{\circ 2} \rangle \approx \frac{\alpha}{\beta} + 0\left(\frac{D}{\alpha}\right). \quad (2.14)$$

When  $\alpha^2/D\beta \ll 1$ ,  $\langle X_s^{\circ 2} \rangle$  becomes

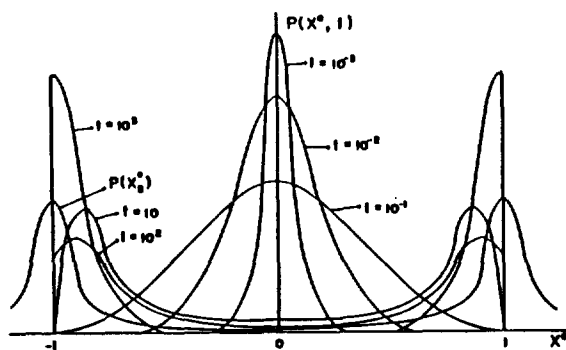


Figure 2. The Dependence of  $P(X^\circ, t)$  on Time [ $\alpha = \beta = 1$ , and  $D = 0.1$ ].

$$\langle X_s^{\circ 2} \rangle = \frac{\alpha}{2\beta} \left[1 + 27 \frac{\Gamma(\frac{3}{4})}{\Gamma(\frac{1}{4})} + \dots\right], \quad (2.15)$$

where  $\Gamma(x)$  is the gamma function.

As expected,  $\langle X_s^{\circ 2} \rangle$  in the case of  $\alpha^2/D\beta \ll 1$  is quite different from the value of  $X_s^{\circ 2}$  based on the rate equation. Thus, we consider only the case that  $\alpha$  is larger than  $\beta$  and the diffusion constant is smaller than  $\beta$ . The average of  $X^\circ(t)$  depending on time is

$$\begin{aligned} \langle X^\circ(t)^2 \rangle &= \int_{-\infty}^{\infty} dX^\circ X^{\circ 2} P(X^\circ, t) = \frac{\alpha}{\beta} (1 - \exp(-\alpha t))^{-1} \\ &\quad Y(\gamma(t)), \end{aligned} \quad (2.16)$$

where the function  $Y$  is defined as

$$\begin{aligned} Y(\gamma(t)) &= 1 - \left(\frac{2}{\gamma(t)}\right)^{1/2} \exp\left(\frac{1}{2\gamma(t)}\right) + \gamma(t)^{-1} + \dots; \\ \gamma(t) &= (4D\beta/\alpha^2) \sinh^2 \alpha t. \end{aligned} \quad (2.17)$$

As time goes to infinity,  $\langle X^\circ(t)^2 \rangle$  corresponds to  $X_s^{\circ 2}$ . The probability average of  $X^\circ(t)^2$  near a stable steady state may be approximately described as

$$\begin{aligned} \langle X^\circ(t)^2 \rangle &\approx X_s^{\circ 2} \left[1 - \left(\frac{2\alpha^2}{D\beta}\right)^{1/2} \exp(-\alpha t)\right] = \\ &\quad X_s^{\circ 2} - \epsilon \exp(-\alpha t); \quad \epsilon = \left(\frac{2\alpha^4}{D\beta^2}\right)^{1/2}. \end{aligned} \quad (2.18)$$

The time average of  $X_s^{\circ 2}$  at a stable steady state is given as follows

$$\overline{X_s^{\circ 2}} = \lim_{t \rightarrow \infty} \overline{X^\circ(t)^2} = \frac{\alpha}{\beta}. \quad (2.19)$$

At a stable steady state the probability average for  $X_s^{\circ 2}$  is the same as  $X_s^{\circ 2}$  and the time average of  $X_s^{\circ 2}$  given by

$$\langle X_s^{\circ 2} \rangle = \overline{X_s^{\circ 2}} = X_s^{\circ 2} = \frac{\alpha}{\beta}. \quad (2.20)$$

We may choose any definition in the above relation to discuss the dynamic properties at a stable steady state. However, with the aid of  $X^\circ(t)$  or the time average of  $X^\circ(t)^2$  we may not discuss the dynamic properties near a stable steady state different from those at a stable steady state, when the system relaxes from the unstable steady state. In such case we shall approximately use the probability average for  $X^\circ(t)^2$ .

#### The Time Correlation Function for the Fluctuating Variables.

In this section we shall discuss time correlation functions at (and near) a stable steady state, when the system relaxes from the unstable steady state. Using the definition of the Fourier transform of a function,  $f(\vec{r}, t)$  with respect to  $\vec{r}$  and its inverse Fourier transform as

$$\begin{aligned} f(\vec{k}, t) &= \int_{\vec{r}} \exp(-i\vec{k} \cdot \vec{r}) f(\vec{r}, t), \\ f(\vec{r}, t) &= \frac{1}{(2\pi)^3} \int_{\vec{k}} \exp(i\vec{k} \cdot \vec{r}) f(\vec{k}, t), \end{aligned} \quad (2.21)$$

eqn. (2.5b) is written as

$$\frac{\partial}{\partial t} x(\vec{k}, t) = -(Dk^2 + 3\beta X^\circ(t)^2 - \alpha) x(\vec{k}, t) + \eta(\vec{k}, t) \quad (2.22)$$

$$-\frac{\beta}{(2\pi)^3} \int_{\vec{k}_1, \vec{k}_2, \vec{k}_3} x(\vec{k}_1, t) x(\vec{k}_2, t) x(\vec{k}_3, t) \delta(\vec{k} - \vec{k}_1 - \vec{k}_2 - \vec{k}_3),$$

$$-\frac{3\beta X^0(t)}{(2\pi)^3} \int_{\vec{k}_1, \vec{k}_2} x(\vec{k}_1, t) x(\vec{k}_2, t) \delta(\vec{k} - \vec{k}_1 - \vec{k}_2)$$

where  $\int_{\vec{k}}$  means  $\int d\vec{k}$ . Let us assume the following Gaussian-conditions

$$\langle x(\vec{k}, 0) \eta(\vec{k}, t) \rangle = 0, \quad (2.23)$$

$$\langle x(\vec{k}, t_1) x(\vec{k}, t_2) \cdots x(\vec{k}, t_n) \rangle =$$

$$\begin{cases} 0, & \text{if } n \text{ is an odd integer,} \\ \text{sum over all the possible pair products,} \\ \text{if } n \text{ is an even integer.} \end{cases}$$

Let us define a time correlation function as

$$G(\vec{k}, t, t') = \langle x(\vec{k}, t) x(\vec{k}', t') \rangle \delta(\vec{k} - \vec{k}'). \quad (2.24)$$

Neglecting the nonlinear terms in eq. (2.22) and using the first condition in eq. (2.23), the time correlation function  $G^0(\vec{k}, t)$  is given as

$$G^0(\vec{k}, t) = \langle x(\vec{k}, t) x(\vec{k}, 0) \rangle = \langle x(\vec{k}, 0)^2 \rangle \exp\left\{-\int_0^t dt' [Dk^2 + 3\beta X^0(t')^2 - \alpha]\right\} \quad (2.25)$$

At a stable steady state the correlation function is

$$G^0(\vec{k}, t) = \langle x(\vec{k}, 0)^2 \rangle \exp[-D(k^2 + \xi^{-2})t], \quad (2.26)$$

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

$$\xi^{-2} = \frac{1}{D} (3\beta X_s^0{}^2 - \alpha) = 2\alpha/D. \quad (2.27)$$

The result at a stable steady state is just the same as the previous result.<sup>9</sup> With the aid of the relation in eq. (2.20) the correlation length at a stable steady state may be defined as follows

$$\xi^{-2} = \frac{1}{D} (3\beta X_s^0{}^2 - \alpha) = \frac{1}{D} (3\beta X_s^0{}^2 - \alpha) = \frac{1}{D} (3\beta \langle X_s^0{}^2 \rangle - \alpha). \quad (2.28)$$

The above relation shows that any definition for the correlation length may be applied at a stable steady state. Near a stable steady state when the system relaxes from the unstable steady state,  $X^0(t)^2$  or  $\overline{X^0(t)^2}$  is independent of time and becomes the value of a stable steady state. Thus, using eq. (2.18) to obtain the correlation function near a stable steady state explicitly, we have

$$G^0(\vec{k}, t) = \langle x(\vec{k}, 0)^2 \rangle \exp[-D(k^2 + \xi(t)^{-2})t], \quad (2.29)$$

where the time-dependent correlation length is

$$\xi(t)^{-2} = \xi^{-2} - (3\beta \epsilon / \alpha t) (1 - \exp(-\alpha t)). \quad (2.30)$$

The exponential term in eq. (2.30) may be neglected. If  $3\beta\epsilon/\alpha t$  is not negligibly small, the above result is different from the previous result<sup>9</sup>, which is just the same as that at the stable steady state. In the case that  $3\beta\epsilon/\alpha t$  is not negligibly small, we may consider that the region where the present result holds is also "near a stable steady state".

Let us calculate the effect of nonlinearity on the correlation function. The time correlation function may be described as follows, using the standard renormalization method

$$G(\vec{k}, t) = \langle x(\vec{k}, 0)^2 \rangle \exp\left\{-\int_0^t dt' D[k^2 + \frac{1}{D} (3\beta X_R^0(t')^2 - \alpha)]\right\}, \quad (2.31)$$

with

$$X_R^0(t) = X^0(t)^2 - \frac{1}{(2\pi)^3} [2X^0(t) \langle x_1(t) \rangle - \frac{\langle x(t)^2 \rangle}{(2\pi)^3}], \quad (2.32)$$

where use has been made of eq. (2.23), the coupling between the nonlinear terms has been neglected and  $x_1(t)$  is defined as

$$x_1(t) = 3\beta \int_0^t dt' G^0(t, t') X^0(t') x(t')^2. \quad (2.33)$$

It should be noted that  $X_R^0(t)^2$  does not depend on  $\vec{k}$ . If the first term in the square bracket of eq. (2.32) is larger (or smaller) than the second term, the effect of nonlinearity increases (or decreases) the correlation length between the fluctuating variables. Taking up to the first order of  $\beta$  and the most dominant term, the correlation function at a stable steady state becomes

$$G(\vec{k}, t) = \langle x(\vec{k}, 0)^2 \rangle \exp[-D(k^2 + \xi_R^{-2})t], \quad (2.34)$$

where the renormalized correlation length is given by

$$\xi_R^{-2} = \xi^{-2} - \frac{9\beta}{16\pi^3\alpha}. \quad (2.35)$$

As shown in eq. (2.35) the renormalized correlation length at a stable steady state is larger than the correlation length obtained by the linear method. It is not possible to calculate the effect of nonlinearity on the time-dependent correlation length exactly. Thus, using the approximation method and taking the most dominant term, we have<sup>12</sup>

$$G(\vec{k}, t) = \langle x(\vec{k}, 0)^2 \rangle \exp[-D(k^2 + \xi_R(t)^{-2})t], \quad (2.36)$$

with

$$\xi_R(t)^{-2} = \xi(t)^{-2} - \frac{9\beta}{16\pi^3\alpha} \exp\left(\frac{6\beta\epsilon}{\alpha}\right), \quad (2.37)$$

where  $X^0(t)^2$  in eq. (2.32) has been replaced by  $\langle X^0(t)^2 \rangle$ . The time dependent correlation length near a stable steady state is increased by the nonlinear terms, whose effect is larger than the correlation length at a stable steady state. This theory may be easily applied to the TDGL model without magnetic field<sup>10</sup> and *etc.*<sup>2</sup>

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## Photocycloaddition Reaction of *trans*-Cinnamionitrile Derivatives with Tetramethylethylene

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Stereospecific [2+2] cycloadducts are obtained as major products when *trans*-cinnamionitrile derivatives are irradiated with excess tetramethylethylene. The fluorescence quenching studies, weak exciplex fluorescence, and sensitization by benzophenone suggest that this stereospecific photochemical cycloaddition reaction involves singlet exciplex intermediate formed between cinnamionitrile derivatives and tetramethylethylene.

### Introduction

The photocycloaddition reactions of compounds which are the type of  $C_6H_5CH=CXY$  with tetramethylethylene (TME) and other olefins have been reported with much attention.<sup>1-3</sup> Thier mechanism usually involves singlet excited state of the  $C_6H_5CH=CXY$  with ground state of olefins giving an exciplex and the stereochemistry of products is retention. The triplet state of the  $C_6H_5CH=CXY$  produced by sensitization gives only *cis*  $\rightleftharpoons$  *trans* isomerization and no cycloadduct is observed from the triplet state.<sup>4</sup>

In order to investigate the mechanism of and the substituent effects on the cycloaddition reaction of *trans*-cinnamionitrile derivatives, fluorescence quantum yields, fluorescence quenching by olefins, and sensitization by benzophenone of the compounds are studied.

### Experimental

**Materials.** *trans*-Cinnamionitrile derivatives (*m*-Br, *m*-Cl, *p*-Cl, *m*-OCH<sub>3</sub>, *p*-OCH<sub>3</sub>, *p*-CH<sub>3</sub>, *m*-NO<sub>2</sub>, *p*-NO<sub>2</sub>) were synthesized from corresponding *trans*-cinnamic acids (Aldrich Chemical Co.) by the method reported.<sup>5</sup> Other *trans*-cinnamionitrile derivatives (*p*-Br, *p*-N, N-dimethyl amino) were synthesized from modified Wittig reaction in which the corresponding benzaldehydes were treated by the carbanion of diethyl cyanomethanephosphonate synthesized from triethyl phosphonate and 2-chloroacetonitrile (Aldrich Chemical Co.).<sup>6,7</sup> These *trans*-cinnamionitrile derivatives were separated by column chromatography and recrystallized from *n*-hexane and methanol. Tetramethylethylene (99+%, gold level) (TME) and methylcrotonate were obtained from Aldrich Chemical Co. and used without further purification. Fumaronitrile was also obtained from Aldrich Chemical Co. and purified by recrystallization and sublimation. All the solvents such as chloroform, methanol, cyclohexane were obtained from Merck Chemical Co..

**Spectra.** <sup>1</sup>H NMR spectra were measured on Varian T-60A and Varian 80A spectrometers against tetramethylsilane internal standard in deuterated chloroform. Ultraviolet-visible spectra were recorded on a Cary 17 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Model 267 spectrophotometer using potassium bromide pellets and/or sodium plate. Fluorescence spectra were recorded on an Aminco-Bowman spectrofluorometer with Aminco XY-recorder.

**Irradiation of *trans*-Cinnamionitrile Derivatives and Tetramethylethylene.** *trans*-Cinnamionitrile and TME in chloroform solution were deoxygenated by bubbling dry nitrogen through the solution for 0.5-1 h and irradiated for 25-50 hrs in a Rayonet Photochemical Reactor (The Southern New England Ultraviolet Co.) Model RPR-208 or RPR-100 equipped with eight 300 nm UV lamps.

Irradiated samples were analyzed by silica gel TLC utilizing *n*-hexane-dichloromethane or *n*-hexane-ethyl ether mixture as a developing solvent. The major product was isolated by preparative TLC.

**Determination of Fluorescence Quantum Yields and Fluorescence Quenching by Olefins.** Fluorescence quantum yields ( $\Phi_f^s$ ) of *trans*-cinnamionitrile derivatives in dilute solution<sup>8</sup> were determined by eq. (1)

$$\frac{\Phi_f^s \cdot OD}{\Phi_f^r \cdot OD} = \frac{\Phi_f^s \epsilon_s c_s d I_0}{\Phi_f^r \epsilon_r c_r d I_0} = \frac{\text{area under fluo. peak}^s}{\text{area under fluo. peak}^r} \quad (1)$$

in which the subscript *s* means *trans*-cinnamionitrile derivatives, *r* means *p*-terphenyl or dimethoxycoumarin (DMC) as references, and OD means the optical density. The approximation of  $cdI_0 \approx I_0$  for OD < 0.05 is used. The relative fluorescence quantum yields of *trans*-cinnamionitrile derivatives were determined by measuring the weight of area under the fluorescence bands.

In order to determine the Stern-Volmer constants ( $k_q \cdot \tau$ ) of fluorescence quenching, the fluorescence spectra of *trans*-