

On the stability of a chain reaction with respect to global and local fluctuations

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1987 J. Phys. A: Math. Gen. 20 5231

(<http://iopscience.iop.org/0305-4470/20/15/036>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 31/05/2010 at 20:51

Please note that [terms and conditions apply](#).

On the stability of a chain reaction with respect to global and local fluctuations

F de Pasquale[†], J Gorecki^{‡§} and J Popielawski^{||}

[†] Department of Physics, Università 'La Sapienza' Roma, Piazzale Aldo Moro 2, I-00185 Roma, Italy

[‡] Department of Chemistry, University of Manchester, Manchester M13 9PL, UK

^{||} Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, PL-01-224 Warszawa, Poland

Received 13 November 1986

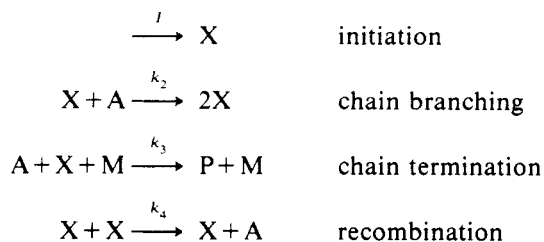
Abstract. The stability of a chain reaction with respect to global and local fluctuations of the reaction parameters is discussed within a linear model for the reaction kinetics. The spatial correlations in the system are studied for the case when the local fluctuations are smaller than the global one. The time dependence of the correlation length is presented.

1. Introduction

It is observed for many chemical reactions that fluctuations lead to the spatial decomposition of the system (Horsthemke and Lefever 1984). In this paper we are concerned with the mathematical analysis of this phenomenon. We describe the chemical reaction using a stochastic reaction-diffusion equation, which is solved within the linear approximation. On the basis of this solution the information on the correlations in the system may be obtained directly from the correlation function or, as is presented in this paper, by the correlation length.

To make our results general we consider a chain reaction (Kondratiev and Nikitin 1981), because this model is widely used for the description of different chemical processes. For example, in the application to the combustion phenomena, where the influence of fluctuations on the behaviour of the system is prominent, the approach based on a chain reaction is called the Zeldovich-Linan model (Peters 1985).

The simplest kinetic scheme for the development of a chain reaction is the following (Kondratiev and Nikitin 1981):



§ Permanent address: Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, PL-01-224 Warszawa, Poland.

where X denotes the molecule of the active component and A, P, M denote molecules of precursor states and the product.

Usually at the early stages of the chain reaction recombination is neglected. When we assume that the system is homogeneous then its time evolution may be described by the following rate equation:

$$\frac{dC_X}{dt} = I + (a - b)C_X \quad (1)$$

$$a = k_2 C_A \quad b = k_3 C_A C_M$$

where C_A , C_M , C_X are the concentrations of A, M and X respectively. In general, a and b depend on the external parameters like temperature or pressure. Usually the rate constant a , which corresponds to the chain branching, depends on temperature more strongly than the rate constant b , which is connected with the chain termination. This means that we can change the sign of $a - b = \alpha$ by changing the temperature of the system. However (see (1)) when $\alpha < 0$ the concentration C_X approaches the stable value, whereas for $\alpha > 0$ the behaviour of the system is explosive. Thus in the neighbourhood of the transition $\alpha = 0$ the system is very sensitive to small changes of the control parameters. Hence it can be expected that fluctuations of the external parameters play an important role. In this respect a system with chain reaction is similar to others where the fluctuations of control parameters are important (Horsthemke and Lefever 1984).

The model of chain reaction can also describe the behaviour of the chemical system near its equilibrium state. Let us assume that the deterministic rate equation, possibly non-linear, is

$$\frac{dC_X}{dt} = F(C_X). \quad (2)$$

If C_{Xe} is an equilibrium state ($F(C_{Xe}) = 0$ and $F'(C_{Xe}) < 0$) then for C_X in the neighbourhood of C_{Xe} the rate equation is

$$\frac{dC_X}{dt} = -C_{Xe}F'(C_{Xe}) + C_XF'(C_{Xe}) \quad (3)$$

(the terms of the orders $(C_X - C_{Xe})^2$ and higher are neglected in (3)). Local fluctuations of temperature can locally change the rate constant and therefore lead to a non-homogeneous spatial distribution of concentration. From the mathematical point of view equations (1) and (3) are identical and the method we present here may be applied to study the correlations in such cases.

2. Homogeneous fluctuations of the reaction rate

To study the influence of homogeneous fluctuations on the behaviour of the system let us assume that the parameter α is a stochastic quantity:

$$\alpha(t) = \alpha_0 + \xi(t) \quad (4)$$

where α_0 is a constant and $\xi(t)$ is a rapidly fluctuating random term. It is convenient to assume that $\xi(t)$ is white noise with dispersion Γ_0

$$\langle \xi(t) \rangle = 0 \tag{5}$$

$$\langle \xi(t)\xi(s) \rangle = \Gamma_0\delta(t-s) \tag{6}$$

where $\langle \dots \rangle$ denotes an average.

Equation (1) is now replaced by the following stochastic differential equation:

$$\frac{dC_X}{dt} = I + \alpha_0 C_X + \xi(t)C_X. \tag{7}$$

The linear stochastic differential equation is widely discussed in the literature (Gardiner 1983) and the general form of its solution is known. However the solution of equation (7) depends on whether it is regarded as an Ito or as a Stratonovich stochastic differential equation (SDE). In the following we will assume that this equation is an Ito SDE, as this interpretation seems to be more justified from the physical point of view. Treating (7) as a Stratonovich SDE we get the unphysical result that $\langle C_X \rangle(t) \sim \exp(\Gamma_0 t/2)$ when $I = 0$ and $\alpha_0 = 0$.

Within the Ito calculus we have the following formulae for the average value of C_X and its dispersion:

$$\langle C_X \rangle(t) = (I/\alpha_0 + C_{X0}) \exp(\alpha_0 t) - I/\alpha_0 \tag{8}$$

$$\begin{aligned} \langle (\delta C_X)^2 \rangle(t) &= \frac{I^2}{\alpha_0^2} \frac{\Gamma_0}{2\alpha_0 + \Gamma_0} \{ \exp[(2\alpha_0 + \Gamma_0)t] - 1 \} \\ &\quad - 2 \frac{I}{\alpha_0} \left(\frac{I}{\alpha_0} + C_{X0} \right) \frac{\Gamma_0}{\alpha_0 + \Gamma_0} \exp(\alpha_0 t) \{ \exp[(\alpha_0 + \Gamma_0)t] - 1 \} \\ &\quad + (I/\alpha_0 + C_{X0})^2 \exp(2\alpha_0 t) [\exp(\Gamma_0 t) - 1] \end{aligned} \tag{9}$$

where C_{X0} denotes the initial concentration of X.

It may be noticed that the stability condition for the $\langle C_X \rangle (\alpha_0 < 0)$ is different from the stability condition for the dispersion ($2\alpha_0 + \Gamma_0 < 0$). It can be easily proved that there is no uniform stability condition for all moments of the random function $C_X(t)$ described by equation (7). For any values of α_0 and Γ_0 ($\Gamma_0 \neq 0$) there exists an integer n such that all the moments of $C_X(t)$ of the order $m (m > n)$ diverge. On the other hand, if the moment $\langle C_X^m(t) \rangle$ is stable then all the moments of lower order are stable too.

To avoid the problem of the stability of the higher moments and to make the mathematical model of a chain reaction more complete it is necessary to include the term corresponding to recombination ($-k_4 C_X^2$, no random character of k_4 assumed) to equation (7). It can be shown that in this case

$$\frac{d\langle C_X^n \rangle}{dt} < n \left[I \langle C_X^{n-1} \rangle + \left(\alpha_0 + \frac{(n-1)}{2} \Gamma_0 \right) \langle C_X^n \rangle - k_4 \frac{\langle C_X^n \rangle^2}{\langle C_X^{n-1} \rangle} \right] \tag{10}$$

which proves that no moments diverge. However equation (7) with the recombination term added is more complicated than the linear one. In the following we will assume that for the processes we are studying the recombination term may be neglected. Therefore in the linear regime $\alpha_0 < 0$ ensures the stability of the average value and $2\alpha_0 + \Gamma_0 < 0$ is the condition for stability of dispersion.

The correlation length is connected with the second moment of concentration (20). Therefore one can expect that when the conditions for stability of dispersion are satisfied then the linear model leads to a reasonable result. On the other hand, when the second moment of C_x is unstable then the linear theory can describe the correlations in the initial period only and the non-linear effects have to be taken into account for the analysis of long time behaviour.

Numerical tests show that when the stability condition for $\langle(\delta C_x)^2\rangle$ is satisfied and when the recombination term is small then equations (8) and (9) well describe the evolution of the system. When $\langle(\delta C_x)^2\rangle$ diverges the non-linear term in equation (9)

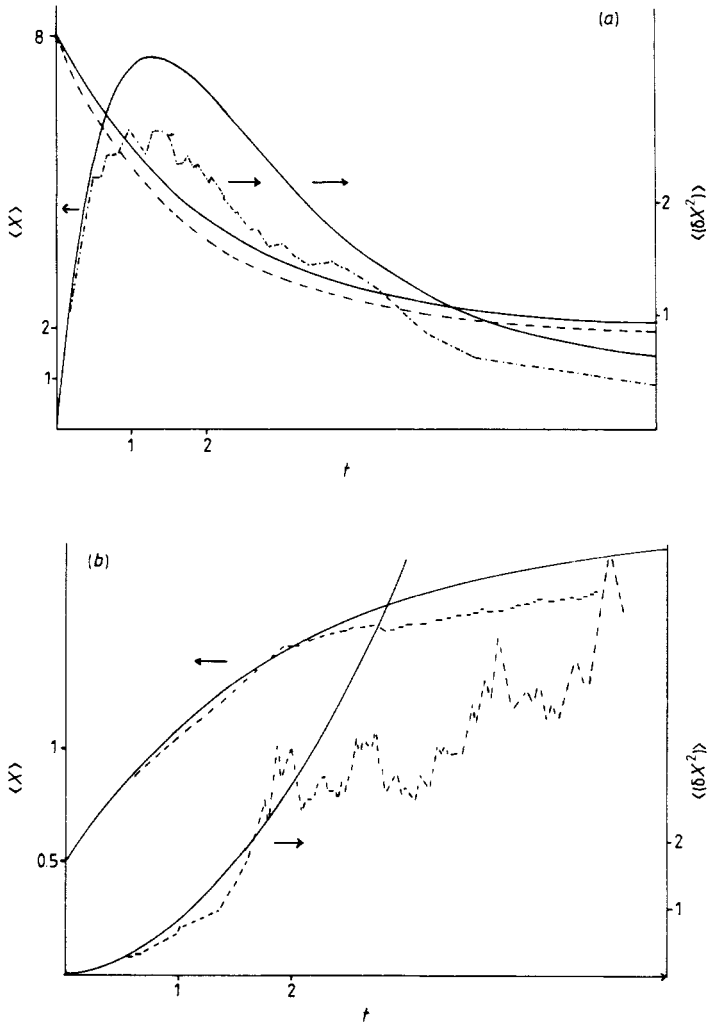


Figure 1. The time evolution of the average concentration $\langle C_x \rangle$ and its dispersion. The comparison of the computer simulation of the stochastic differential equation (broken curve):

$$x = I + (\alpha_0 + \xi(t))x - \epsilon x^2 \quad (I = 1, \alpha_0 = -0.5, \epsilon = 0.01)$$

with the linear Ito stochastic differential equation ($\epsilon = 0$, full curve). (a) Stable case ($\Gamma_0 = \frac{1}{5}$, 800 equations). (b) Unstable case ($\Gamma_0 = 1.11$, 4000 equations).

plays an important role, but the evolution of the system in the initial period can be also well approximated using equations (8) and (9). The comparison of the computer simulation of 800 and 4000 stochastic differential equations $X = I + (\alpha_0 + \xi(t))X - \varepsilon X^2$ with the results obtained from equations (8) and (9) is presented in figure 1.

3. Non-homogeneous fluctuations

The model of the kinetics of the chain reaction with a fluctuating reaction rate can be generalised to include noise-induced spinodal decomposition. Now the evolution of the system is governed by a stochastic reaction-diffusion equation:

$$\frac{dC_X(r, t)}{dt} = I + \alpha_0 C_X(r, t) + \xi(r, t)C_X(r, t) + D\nabla^2 C_X(r, t) \tag{11}$$

where $C_X(r, t)$ describes the local concentration of X , $\xi(r, t)$ is the local noise and D is the diffusion coefficient. To write equation (11) it is necessary to assume that the concentrations of A and M are homogeneous and constant.

Let us assume that both $C_X(r, t)$ and $\xi(r, t)$ can be described as a sum of homogeneous and non-homogeneous terms and that the first one plays the more important role:

$$C_X(r, t) = C_X(t) + \tilde{C}_X(r, t) \tag{12}$$

where $\tilde{C}_X(r, t) \ll C_X(t)$ and

$$\xi(r, t) = \xi(t) + \tilde{\xi}(r, t)$$

where

$$\langle \xi(t)\xi(s) \rangle = \Gamma_0 \delta(t-s) \tag{13}$$

$$\langle \tilde{\xi}(r, t)\tilde{\xi}(u, s) \rangle = \Gamma \delta(t-s)\delta(r-u).$$

The assumption that the non-homogeneous part of $C_X(r, t)$ is small is justified when we study the growth of local fluctuations of concentration in the initial period of a reaction starting from a homogeneous state.

Substituting (12) and (13) into (10) we obtain

$$\frac{dC_X}{dt} = I + (\alpha_0 + \xi(t))C_X \tag{14}$$

and

$$\frac{d\tilde{C}_X(r, t)}{dt} = (\alpha_0 + \xi(t))\tilde{C}_X(r, t) + D\nabla^2 \tilde{C}_X(r, t) + \tilde{\xi}(r, t)C_X(t). \tag{15}$$

From the inequality $\tilde{C}_X(r, t) \ll C_X(t)$ it follows that $\tilde{\xi}(r, t)\tilde{C}_X(r, t) \ll \tilde{\xi}(r, t)C_X(t)$ and therefore the term $\tilde{\xi}(r, t)\tilde{C}_X(r, t)$ is neglected in (15). As might be expected the local fluctuations of the parameters of reaction act as a source for local fluctuations of C_X .

Taking the Fourier transform of (15) we obtain

$$\frac{d\tilde{C}_X(q, t)}{dt} = (\alpha_0 + \xi(t) - Dq^2)\tilde{C}_X(q, t) + C_X(t)\tilde{\xi}(q, t) \tag{16}$$

where $\langle \tilde{\xi}(q, t)\tilde{\xi}(p, s) \rangle = \Gamma/(2\pi)^d \delta(q+p)\delta(t-s)$ and d denotes the dimension of space.

It is obvious that $\langle \tilde{C}_x(q, t) \rangle = 0$. From equation (16) we have the following formula for the correlation function $\langle \tilde{C}_x(p, t) \tilde{C}_x(q, t) \rangle$

$$\langle \tilde{C}_x(p, t) \tilde{C}_x(q, t) \rangle = \Gamma / (2\pi)^d \delta(q + p) \int_0^t ds \exp[(2\alpha_0 + \Gamma_0 - 2Dq^2)(t - s)] \langle C_x(t)^2 \rangle. \tag{17}$$

When $2\alpha + \Gamma_0 > 0$ a phenomenon analogous to a spinodal decomposition in phase transition appears (Gunton *et al* 1983). The Fourier components of $C_x(r, t)$ with the wavevector q shorter than the critical value

$$q = \left(\frac{2\alpha_0 + \Gamma_0}{2D} \right)^{1/2} = 1/l_c \tag{18}$$

will grow with time. This means that a local fluctuation which extended over a region of a typical size larger than l_c will grow. The condition for the stability of the system against local fluctuations $2\alpha_0 + \Gamma_0 < 0$ is the same as the condition for stability of the system with respect to the global fluctuations. It may be noticed that the strength of local fluctuations (Γ) has no influence on the stability condition, but in our model this is the consequence of neglecting the term $\xi(q, t) \tilde{C}_x(q, t)$ in equation (15). Within the model presented the dispersion of the local noise only scales the correlation function.

Taking the inverse Fourier transform of (17) we obtain the correlation function in the real space:

$$\begin{aligned} S(r, u, t) &= \langle C_x(r, t) C_x(u, t) \rangle - \langle C_x(r, t) \rangle \langle C_x(u, t) \rangle \\ &= \langle (\delta C_x)^2 \rangle(t) + \langle \tilde{C}_x(r, t) \tilde{C}_x(u, t) \rangle \\ &= \langle (\delta C_x)^2 \rangle(t) + \frac{\Gamma}{(2\pi)^d} \int_0^t ds \langle C_x(s)^2 \rangle \left(\frac{\pi}{2D(t-s)} \right)^{d/2} \\ &\quad \times \exp\left((2\alpha_0 + \Gamma_0)(t-s) - \frac{(r-u)^2}{8D(t-s)} \right). \end{aligned} \tag{19}$$

The propagation of spatial correlation in the system can be characterised by the time-dependent correlation length $l(t)$ defined as

$$l^2(t) = \frac{\int dx dy S(x, y, t) (x-y)^2}{\int dx dy S(x, y, t)}. \tag{20}$$

In our case the correlation length can be written as the sum of two terms connected with the contribution from local and global fluctuations:

$$\begin{aligned} l^2(t) &= \frac{1}{G(t)} \int dx dy (x-y)^2 \langle (\delta C_x)^2 \rangle(t) \\ &\quad + \frac{4D d\Gamma V}{G(t)} \int_0^t ds (t-s) \langle C_x(s)^2 \rangle \exp[(2\alpha_0 + \Gamma_0)(t-s)] \end{aligned} \tag{21}$$

where

$$G(t) = V^2 \langle (\delta C_x)^2 \rangle(t) + V\Gamma \int_0^t ds \langle C_x(s)^2 \rangle \exp[(2\alpha_0 + \Gamma_0)(t-s)]$$

and V is the volume of the system.

Let us notice that when $\langle(\delta C_x)^2\rangle$ is very small then for time $t \rightarrow 0$ formula (21) gives

$$l^2(t) = 2D dt. \tag{22}$$

If we assume that $\langle(\delta C_x)^2\rangle$ may also be neglected for long times and that $\langle C_x^2\rangle$ is constant (which is a quite crude approximation within our theory) then the correlation length is given by

$$l^2(t) = 4D d\left(\frac{t}{1 - \exp[-(2\alpha_0 + \Gamma_0)t]} - \frac{1}{2\alpha_0 + \Gamma_0}\right). \tag{23}$$

It is worthwhile mentioning that the results (22) and (23) predict the same character of growth for the local correlation as was observed for the case of local fluctuations in the TDGL model (de Pasquale *et al* 1985).

However, if we include the first term of (21) the situation is different. Our system is homogeneous for $t = 0$ and if there is no local fluctuations it will remain homogeneous all the time. In the homogeneous system the correlation length is of the order of the system dimension. The presence of local fluctuations destroys the homogeneity and it can reduce the correlations. To discuss the time behaviour of the correlation length let us apply formula (21) in the case when the average value of the concentration in the system is constant ($C_{x0} = -I/\alpha_0$). Then

$$\begin{aligned} l^2(t) = & \frac{\int dr r^2}{V} \left\{ \Gamma_0 \{1 - \exp[-(2\alpha_0 + \Gamma_0)t]\} + \frac{4Dd\Gamma}{\int dr r^2} \right. \\ & \times \left[\frac{t^2\Gamma_0}{2} + \frac{2\alpha_0}{2\alpha_0 + \Gamma_0} \left(t - \frac{1 - \exp[-(2\alpha_0 + \Gamma_0)t]}{2\alpha_0 + \Gamma_0} \right) \right] \left. \right\} \\ & \times \left[\Gamma_0 \{1 - \exp[-(2\alpha_0 + \Gamma_0)t]\} + (\Gamma/V) \right. \\ & \times \left. \left(\Gamma_0 t + 2\alpha_0 \{1 - \exp[-(2\alpha_0 + \Gamma_0)t]\} / (2\alpha_0 + \Gamma_0) \right) \right]^{-1}. \tag{24} \end{aligned}$$

The first term describes the correlation length of the homogeneous system and the following shows its change caused by the local fluctuations. Usually

$$\int dr r^2 \sim VV^{2/d} \quad \text{and} \quad \frac{\Gamma}{V} \gg \frac{\Gamma}{\int dr r^2}.$$

When the system is in the stable state ($2\alpha_0 + \Gamma_0 < 0$) then

$$l^2(t \rightarrow \infty) = \frac{\int dr r^2}{V} \frac{\Gamma_0}{\Gamma_0 + 2\alpha_0\Gamma/[V(2\alpha_0 + \Gamma_0)]}. \tag{25}$$

This result says that the system approaches a new stable state where the correlations are disturbed by the presence of non-local fluctuations and so the correlation length is shorter.

When applying formula (24) to the case of unstable state ($2\alpha_0 + \Gamma_0 > 0$) we first observe the decrease of the correlation length. However, for long times the term proportional to t^2 in the denominator of (24) becomes more important and then the square of the correlation length is proportional to time. This result is a consequence of the formula (19) for the correlation function, which says that in the unstable state the correlations between two distant points increase in time. However this result is

obtained assuming that $C_x(t) \gg \tilde{C}_x(r, t)$, which condition is not satisfied in the unstable case for long time. A more careful analysis involving the term $\tilde{\xi}(r, t)\tilde{C}_x(r, t)$ is necessary to make the description complete.

The comparison of the theory presented above with the numerical simulations of one-dimensional stochastic systems are presented in figure 2. The one-dimensional array of 60 points with the periodic boundary conditions has been chosen as the reference system. Of course, formula (24) applies to the infinite system and its use for the finite one is an approximation. For the system in the stable state the agreement is reasonable. For the unstable system both results are close in the initial period only and then formula (24) fails predicting the correlation length higher than in the homogeneous case which might be connected with the fact that (24) applies for the infinite systems. Nevertheless it is worthwhile to notice that the linear theory predicts at least qualitatively the changes of correlation length caused by non-homogeneous noise.

Concluding our discussion we would like to mention that the chain mechanism of chemical reaction is characteristic for many fast chemical processes such as, for example, explosions at low temperatures and pressures (Kondratiev and Nikitin 1981). The simple stochastic model presented above predicts the non-equilibrium character of evolution as well as some insight into the noise-induced spatial disorder.

It seems that this model can also describe the spatial decomposition in the laser-heated systems. It is known that the power of laser radiation fluctuates (Degiorgio 1982) and therefore the laser is an excellent source of external fluctuations. As far as

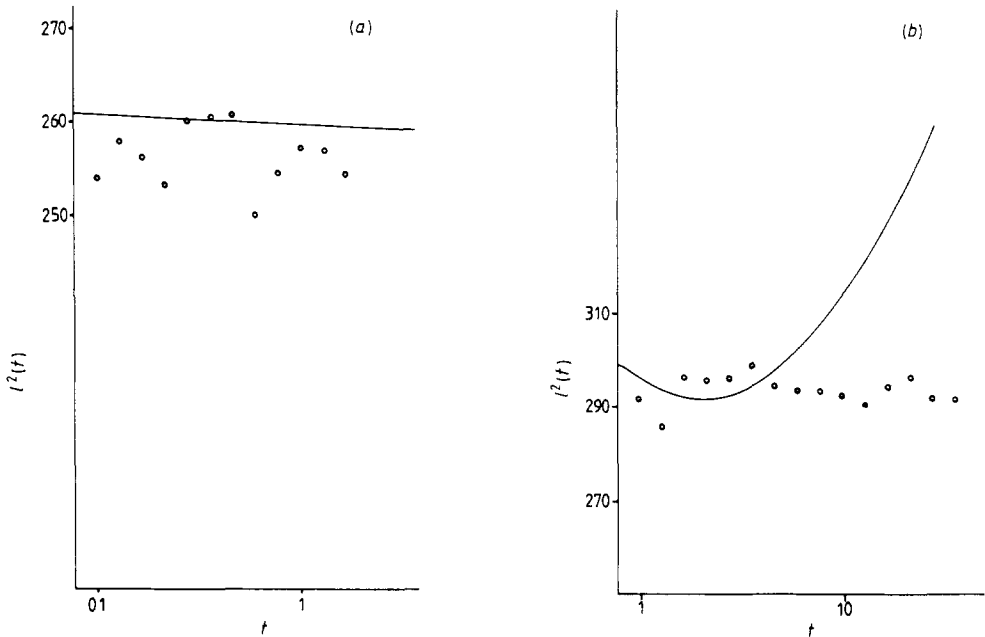


Figure 2. The time evolution of the correlation length of one-dimensional array of 60 points with the periodic boundary conditions (full curve, result of formula (22); open circles, computer simulation). (a) Stable case ($\Gamma_0 = \frac{1}{5}$, $\Gamma = 1$, $D = 1$). (b) Unstable case ($\Gamma_0 = 4$, $\Gamma = 1$, $D = 20$). The square of the correlation length of the homogeneous system is 300. The estimated statistical error of the correlation length is 10 units for (a) and 5 units for (b).

we know the spatial decomposition may be observed when the reagents in a diamond anvil cell are heated with the use of laser radiation.

References

- Degiorgio V 1982 *Nonlinear Phenomena at Phase Transitions and Instabilities* ed T Riste (New York: Plenum) p 181
- de Pasquale F, Tartaglia P and Tombesi P 1985 *Phys. Rev. A* **31** 2447-53
- Gardiner C W 1983 *Handbook of Stochastic Methods* (Berlin: Springer)
- Gunton J D, San Miguel M and Sahni P S 1983 *Phase Transitions and Critical Phenomena* vol 8, ed C Domb and J L Lebowitz (New York: Academic) p 267
- Horsthemke W and Lefever R 1984 *Noise-induced Transitions* (Berlin: Springer)
- Kondratiev V N and Nikitin E E 1981 *Gas-Phase Reactions* (Berlin: Springer)
- Peters N 1985 *Numerical Simulation of Combustion Phenomena* ed R Glowinski, B Larroutourou and R Telman (Berlin: Springer) p 90