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On the growth of range of spatial correlations in isothermal explosion processes

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Abstract. The formula for the correlation length in a system described by a stochastic reaction-diffusion equation (Ito) has been derived on the basis of the small-noise expansion method. The method has been applied to study spatial correlation of isothermal chemical explosion processes in the presence of small non-homogeneous fluctuations of external control parameters. A good agreement with the results of computer simulations of one-dimensional systems with quadratic dynamics has been obtained.

Stochastic reaction-diffusion equations (Gardiner 1983) can be used to describe the behaviour of systems with chemical reactions when the external control parameters such as pressure or temperature are fluctuating. In this paper we present a simple method based on the small-noise expansion which allows us to study the time evolution of spatial correlations in such systems. The technique discussed below may be applied, for example, to describe a chemical explosion in a well stirred system, where small local fluctuations of control parameters can be regarded as a perturbation.

For simplicity let us consider a single-component system. Its state at time t is defined if we know the concentration of chemical substance at any point of space $\bar{x}$ $\varphi(\bar{x}, t)$. Let us assume that the time evolution of $\varphi(\bar{x}, t)$ is described by the Ito stochastic differential equation (SDE):

$$\mathrm{d}\varphi = F(\varphi)\,\mathrm{d}t + D\nabla^2\varphi\,\mathrm{d}t + \gamma^{1/2}G(\varphi)\xi(\bar{x}, t)\,\mathrm{d}t \tag{1}$$

where $F(\varphi)$ is a function of concentration which represents the production of X by local processes, D is a diffusion coefficient and $G(\varphi)$ is a function of the local density which relates the local fluctuations with the rate of reaction. $\xi(\bar{x}, t)$ is local white noise with the usual properties:

$$\langle\xi(\bar{x}, t)\rangle = 0 \qquad \langle\xi(\bar{x}, t)\xi(\bar{y}, s)\rangle = \delta(\bar{x}-\bar{y})\delta(t-s).$$

The parameter γ describes the strength of noise and in the following we will assume that it is small enough to justify the small-noise expansion (Gardiner 1983).

If the initial state is homogeneous then it becomes non-homogeneous because of non-homogeneous noise in the system. For the case of an homogeneous initial state, the solution $\varphi(\bar{x}, t)$ may be expanded in the powers of $\gamma^{1/2}$ in the following way:

$$\varphi(\bar{x}, t) = \varphi_0(t) + \gamma^{1/2}g(\bar{x}, t) + \gamma h(\bar{x}, t) + \ldots \tag{2}$$

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where φ_0 does not depend on $\bar{x}$. The actual meaning and validity of such an expansion is not trivial. A general discussion of this problem can be found in Gardiner's book (1983). The small noise expansion seems to be sensible only for special functionals F and initial states φ_0^0; however, the range of its validity is, as far as we know, yet unanswered. It can be shown (de Pasquale *et al* 1986) that the small noise expansion gives an unphysical long-time behaviour when the system is initially in an unstable state, because small fluctuations are amplified in time and the method is divergent. In the following we discuss this example and our method fails to predict the correlation length for long times (equation (11) and following text). On the other hand the small-noise expansion seems to be justified when the dynamics F and the initial state φ_0^0 ensure the convergence to the stable state. Having in mind the limitations of the method we can write the approximation (2) of the solution φ which takes into account the terms up to the first order in γ.

Substituting (2) into (1) we obtain

$$\mathrm{d}\varphi_0 = F(\varphi_0)\,\mathrm{d}t \tag{3a}$$

$$\mathrm{d}g = \left[\left(\frac{\partial F}{\partial \varphi}\right)\bigg|_{\varphi=\varphi_0} g + D\nabla^2 g\right]\mathrm{d}t + G(\varphi_0(t))\xi(x,t)\,\mathrm{d}t \tag{3b}$$

and similarly equations corresponding to the higher terms in (2) may be obtained (see, e.g., Gardiner (1983) equation (6.2.6)). We note that equation (3a) does not involve any stochastic term; it is deterministic and may be directly integrated. The correlation function in stochastic systems is defined as (Gardiner 1983):

$$S(\bar{x},\bar{y},t) = \langle\varphi(\bar{x},t)\varphi(\bar{y},t)\rangle - \langle\varphi(\bar{x},t)\rangle\langle\varphi(\bar{y},t)\rangle \tag{4}$$

and if we consider terms up to the order of γ then it becomes

$$S(\bar{x},\bar{y},t) = \gamma\langle g(\bar{x},t)g(\bar{y},t)\rangle \tag{5}$$

because terms containing the function h cancel in (4). The function g can be easily calculated in momentum space. Calculating the Fourier transform of both sides of (3b) we obtain

$$\mathrm{d}g(\bar{q},t) = \left[\left(\frac{\partial F}{\partial \varphi}\right)\bigg|_{\varphi=\varphi_0} g(\bar{q},t) - Dq^2 g(\bar{q},t)\right]\mathrm{d}t + G(\varphi_0(t))\xi(\bar{q},t)\,\mathrm{d}t \tag{6}$$

and the Fourier components of the noise $\xi(\bar{x},t)$ satisfy: $\langle\xi(\bar{p},t)\xi(\bar{q},s)\rangle = \delta(\bar{q}+\bar{p})\delta(t-s)$. The equation (6) is a linear Ito SDE and it may be directly integrated (Gardiner (1983) equation (4.4.69)). A straightforward calculation gives the following expression for the correlation function:

$$S(\bar{x},\bar{y},t) = \frac{\gamma}{(2\pi)^d}\int \mathrm{d}\bar{p}\,\mathrm{d}\bar{q}\langle g(\bar{p},t)g(\bar{q},t)\rangle \exp[-\mathrm{i}(\bar{p}\bar{x}+\bar{q}\bar{y})]$$

$$= \frac{\gamma}{(2\pi)^{d/2}}\int_0^t \mathrm{d}s \frac{F^2(\varphi_0(t))}{F^2(\varphi_0(s))}\frac{G^2(\varphi_0(s))}{[4D(t-s)]^{d/2}}\exp\left(-\frac{(\bar{x}-\bar{y})^2}{8D(t-s)}\right) \tag{7}$$

where d denotes the dimension of space where the reaction occurs; $\bar{x}\in\mathbb{R}^d$. $S(\bar{x},\bar{y},t)$ describes the average correlations between the local concentration of X in different points of a system. The global characteristic of the range of correlations is described by the correlation length $l(t)$, which is defined as:

$$l^2(t) = \frac{\int \mathrm{d}\bar{x}\,\mathrm{d}\bar{y}\,|\bar{x}-\bar{y}|^2 S(\bar{x},\bar{y},t)}{\int \mathrm{d}\bar{x}\,\mathrm{d}\bar{y}\,S(\bar{x},\bar{y},t)}. \tag{8}$$

Substituting $S(\bar{x}, \bar{y}, t)$ from (7) into (8) we obtain

$$l^2(t) = 4Dd\left(t - \frac{\int_0^t \mathrm{d}s\, sG^2(\varphi_0(s))F^{-2}(\varphi_0(s))}{\int_0^t \mathrm{d}s\, G^2(\varphi_0(s))F^{-2}(\varphi_0(s))} \right). \tag{9}$$

Therefore the small-noise expansion leads to a general formula for correlation length, which expresses it as a function of the deterministic solution $\varphi_0(s)$, the deterministic dynamics F and the character of the noise G. It is worthwhile noting that the correlation length does not depend on the strength of the noise γ, which is a consequence of taking into account only the lowest-order term in the small-noise expansion.

The assumption that there is one-to-one correspondence between the time and the homogeneous concentration φ_0 has been used to derive formula (9). However, when our initial state is a stationary one, i.e. $F(\varphi_0) = 0$, this assumption is not valid. In this case both functions φ_0 and $G(\varphi_0(t))$ in equation (6) are constant and an elementary calculation shows that

$$S(\bar{x}, \bar{y}, t) = \frac{\gamma\beta^2}{(2\pi)^{d/2}} \int_0^t \mathrm{d}s \frac{\exp[2\alpha(t-s) - (\bar{x}-\bar{y})^2/8D(t-s)]}{[4D(t-s)]^{d/2}} \tag{10}$$

where $\alpha = (\partial F/\partial\varphi)|_{\varphi=\varphi_0}$ and $\beta = G(\varphi_0)$. Then the correlation length is given by the formula

$$l^2(t) = 4dD\left(\frac{t}{1-\mathrm{e}^{-2\alpha t}} - \frac{1}{2\alpha} \right). \tag{11}$$

It may be noticed that formula (11) is identical with the result obtained for the early stage relaxation of the one-dimensional time-dependent Ginzburg-Landau (TDGL) model by de Pasquale *et al* (1985). The unlimited linear growth of the correlation length for $\alpha > 0$ when $t \to \infty$, given by (11) is, however, unphysical. In this case the initial state is an unstable stationary state and the small-noise expansion fails, being divergent for long times.

Now let us apply formula (9) to the case of a stochastic reaction-diffusion equation with multiplicative noise, $G(\varphi) = \varphi$. Such equations have been used to model the stochastic behaviour of an explosive reaction (Chandler and Deutch 1983).

In the simplest case the dynamics F is a linear function of φ

$$F(\varphi) = a + b\varphi. \tag{12}$$

When the homogeneous initial state is $\varphi(x, t=0) = \varphi_0^0$ then formula (11) gives:

$$l^2(t) = 4Dd\left(\frac{t^2}{2} + \frac{2a(1-bt-\mathrm{e}^{-bt})}{(b\varphi_0^0+a)b^2} - \frac{a^2(1-2bt-\mathrm{e}^{-2bt})}{4b^2(b\varphi_0^0+a)^2} \right)$$
$$\times \left(t - \frac{2a(1-\mathrm{e}^{-bt})}{(b\varphi_0^0+a)b} + \frac{a^2(1-\mathrm{e}^{-2bt})}{2b(b\varphi_0^0+a)^2} \right)^{-1}. \tag{13}$$

It is easy to see that for short times the increase of correlation length is proportional to the square root of time

$$l^2(t) = 2dDt \tag{14}$$

and is exactly the same rate of growth as it is for SDE with the additive noise (equation (11)). The long-time behaviour depends on the sign of b. When $b > 0$ (explosive behaviour) then a long-time behaviour of correlation length is also given by formula

(14). For $b<0$ the correlation length approaches a constant value $l_x^2 = -2dD/b$ when $t \to \infty$. It follows from (13) that when $(b/a)\varphi_0^0 + 1 > 0$ then $l^2(t)$ grows monotonically, whereas for $(b/a)\varphi_0^0 + 1 < 0$ it has a maximum and then decreases to its stable value. The behaviour of correlation length for the system with linear dynamics as a function of time is shown in figure 1.

A non-linear dynamics is usually more appropriate for modelling the transition from an unstable to a stable state. For example, it allows us to take recombination into account in a chemical reaction. Let us consider the quadratic dynamics:

$$F(\varphi) = a + b\varphi - c\varphi^2. \tag{15}$$

The deterministic solution $\varphi_0(t)$ is

$$\varphi_0(t) = \frac{2a(1-e^{ft}) - \varphi_0^0[f - b + (f+b)\,e^{ft}]}{(b - 2c\varphi_0^0)(e^{ft}-1) - f(e^{ft}+1)} \tag{16}$$

where $f = (b^2 - 4ac)^{1/2}$. The correlation length is then obtained by a direct integration from (9). The results for a few values of parameters are presented in figure 2. In this case, as for that of linear dynamics, the local maximum of correlation length may be also observed.

The appearance of a local maximum of the correlation length represents a qualitatively new effect connected with transient behaviour. It has been observed in recent studies on kinetics of phase transitions (Mazenko and Zanetti 1984, de Pasquale and Tartaglia 1986).

Computer simulations of a system with dynamics (15) have been performed to test the accuracy of the model based on the small-noise expansion. A one-dimensional array of 31 points with periodic boundary conditions has been considered with the

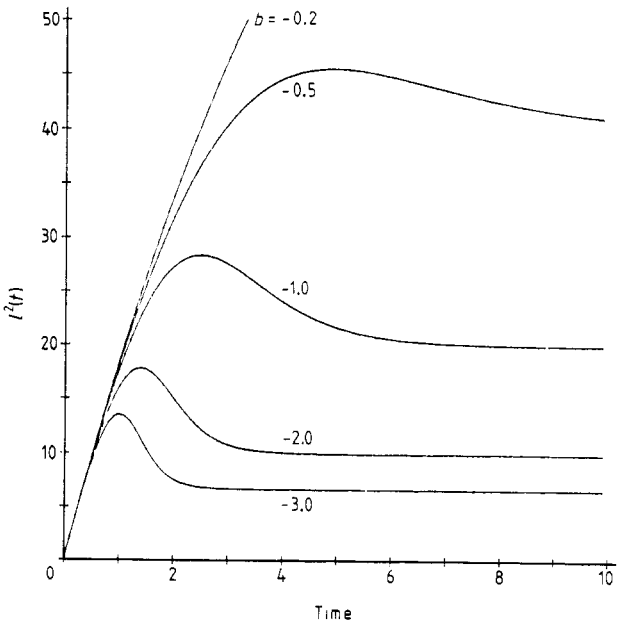

Figure 1. The correlation length as a function of time for the case of linear dynamics plotted as equation (13) with $a = 1$, $\varphi_0^0 = 4$, $d = 1$, $D = 10$ and various values of b.

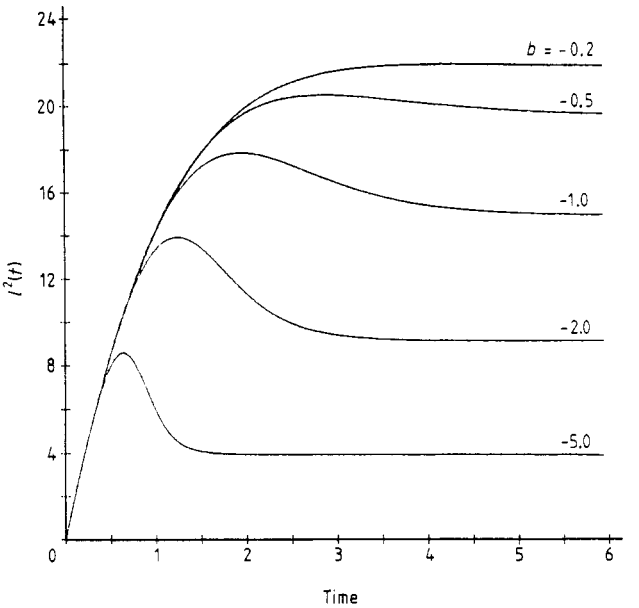

Figure 2. The correlation length as a function of time for the case of quadratic dynamics plotted as equation (16) with $a = 1$, $c = 0.2$, $\varphi_0^0 = 4$, $d = 1$, $D = 10$ and various values of b.

evolution given by the equation

$$\frac{d\varphi_i}{dt} = (a + b\varphi_i - c\varphi_i^2) + D(\varphi_{i-1} - 2\varphi_i + \varphi_{i+1}) + \gamma^{1/2}\varphi_i\xi_i(t). \tag{17}$$

We have used a simplified version of the numerical algorithm developed by Rao *et al* (1974) taking account of terms up to the order of the elementary time interval. A similar first-order algorithm was applied to a Stratonovich SDE with multiplicative noise by Sancho *et al* (1982). Simulation of 9000 systems has been carried out simultaneously. A small size of system (only 31 points) is preferable from the numerical point of view. For distance points the correlation function is close to zero; however, its fluctuations can have a big influence on the correlation length because they are multiplied by the square of distance (equation (8)). Therefore a reliable result for the correlation length may be extracted from the simulation data if the correlation function is known with high accuracy. This can be achieved when a large ensemble is considered, or when the maximal distance is small thus reducing the contribution of distant points to $l(t)$, or finally when a cutoff in the integral in the numerator of (8) is introduced. For the system we used, the ensemble was large enough to give the correlation length without such an artificial cutoff. The simulations have been done for a few values of parameters a, b, c and γ. In general there is a good agreement between the correlation length given by formula (9) and that obtained from the average over the ensemble. Typical results are presented in figure 3. It may be noticed that for the range of parameters used in simulations the strength of noise has no significant influence on the correlation length, as is predicted by the small-noise expansion.

As a final comment we would like to say that the small-noise expansion proved to be a promising approach to the problem of correlation range in stochastic systems. The simple analytic approach predicts an anomalous behaviour of the correlation

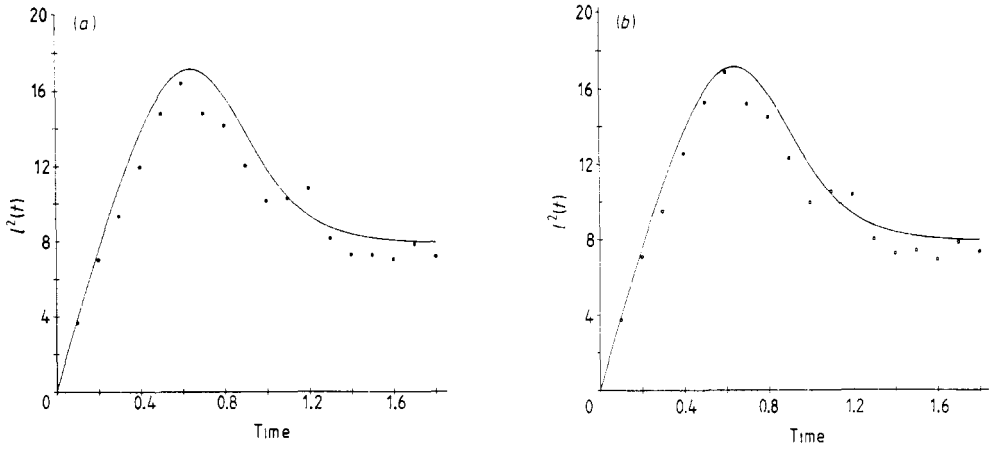

Figure 3. The correlation length in a one-dimensional stochastic system, comparing equation (9) (curve) with a computer simulation (circles) using parameters $a = 1$, $b = -5$, $c = 0.2$, $\varphi_0^0 = 4$, $D = 20$ and (*a*) $\gamma = 2.0$, (*b*) $\gamma = 0.2$.

length, which is confirmed by numerical simulation. It would be interesting to see if the transient maximum of correlation range is observed in experiments.

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