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On the stochastic correlations in a randomly perturbed chemical front

F de Pasquale†, J Gorecki‡ and J Popielawski‡

† Department of Physics, Universita di L'Aquila, I-67100 L'Aquila, Italy
‡ Institute of Physical Chemistry, Polish Academy of Sciences, PL-01-224 Warsaw, Kasprzaka 44/52, Poland

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Abstract. A stochastic reaction-diffusion equation, which describes the time evolution of a front of concentration in a chemical system characterized by a single active component and influenced by the presence of external noise, is solved within the small noise approximation. The spatial correlations of concentration are studied. The relationship between the spectrum of the evolution operator and the correlation function is discussed and two examples (the trigger wave and the wave between a stable and an unstable state) are discussed.

1. Introduction

Front propagation is one of the possible relaxation mechanisms in a non-homogeneous system such that part of it is in a metastable or unstable state and another part is in a stable state. This phenomenon has been encountered in many situations in chemistry (for example in cold flame propagation (Zeldovich *et al* 1980) and in the well known Belousov–Zhabotynski reaction (Showalter *et al* 1979)), biology (nerve conduction (Rinzel and Keller 1973)) and in many other areas of science (Pelce 1988).

In this paper we restrict our attention to chemical systems, which can be completely described by the concentration of a single active component. In the following we denote this concentration by n. It has been established in the pioneering mathematical work on front propagation (Kolmogoroff *et al* in 1937) that the travelling front between a metastable state and a stable state propagates with a unique velocity. Stable and metastable states may coexist if a chemical dynamic $W(n)$ is described by a polynom of the third (or higher) order in the concentration:

$$W(n) = -E(n-m_1)(n-m_2)(n-m_3). \tag{1}$$

However, a rich variety of interesting phenomena may also be observed for a simpler dynamic, which can be described by a polynom of the second order in n:

$$W(n) = I + \alpha n - \beta n^2. \tag{2}$$

For example, the quadratic dynamic describes a quite popular chain reaction (Kondratiev and Nikitin 1981), which consists of the following four elementary processes:

$$\begin{aligned} &\xrightarrow{I} X && \text{initiation}\\ X+A &\xrightarrow{k_2} 2X && \text{chain branching}\\ A+X+M &\xrightarrow{k_3} P+M && \text{chain termination}\\ X+X &\xrightarrow{\beta} X+A && \text{recombination} \end{aligned}$$

where X denotes the molecule of the active component, and A, P, M describe molecules of precursors and product. For the chain reaction the parameter α in equation (2) denotes $k_2[A]-k_3[A][M]$. In such an approach it is assumed that the reagents A and M are in excess, so their concentrations $[A]$ and $[M]$ are homogeneous and time independent. The dynamics (2) may have two stationary states, one stable and another unstable. It may be shown that in this case the travelling front velocity is no longer unique and a new phenomenon appears—the dynamic selection of the front velocity. This subject was studied by Zeldovich (1948) and more recent results in this field have been obtained by Dee and Langer (1983), Ben-Jacob *et al* (1985) and by Van Saarloos (1988).

The aim of this paper is to study the correlations of concentration which may appear when the travelling front is influenced by the external noise. This problem is closely connected to the problem of front stability. Some interesting results in this field for the so-called Schlogl's second model of chemical reaction, for which the dynamic is given by equation (1), were published by Schlogl and Berry (1980), Magyari (1982) and Schlogl *et al* (1983). Here we present some, we hope, new results for the stability of a front between an unstable and a stable state for dynamics (2). Our attention is focused on the stability of a special analytical solution for such a front, which was first given by Kaliappan (1984).

We also derive a formula for the correlation function of concentration in a front, which is perturbed by the presence of the external noise. Our approach is based on the small noise expansion technique and the results are slightly more general than those obtained by Mikhailev *et al* (1983), Schimansky-Geier *et al* (1983) and Engel (1985). A general discussion of the application of the small noise expansion technique is presented in section 2, whereas section 3 is concerned with chemical fronts for the dynamics (1) and (2).

2. The concentration correlation function

Let us consider a chemical system in which the concentration of an active chemical component $n(\boldsymbol{r}, t)$ is a function of time t and position $\boldsymbol{r}\in\mathbb{R}^N$. The time evolution of concentration is governed by the following reaction–diffusion equation:

$$\frac{\partial n}{\partial t}=W(n)+D\nabla^2 n \tag{3}$$

where D is the diffusion constant.

Now let us assume that the system has been influenced by the presence of an external noise η since $t=0$. The time evolution of $n(\boldsymbol{r}, t)$ is now described by the stochastic reaction-diffusion equation

$$\frac{\partial n}{\partial t}=W(n)+D\nabla^2 n+\varepsilon^{1/2}G(n)\eta(\boldsymbol{r},t) \tag{4}$$

where $G(n)$ and ε describe the character and the strength of the noise.

In the following we focus our attention on systems in which $n(\boldsymbol{r},t)$ is a non-uniform function along one direction in space (the variable corresponding to this direction is denoted by x_1). We assume that asymptotically (i.e. for x_1 going to plus and minus infinity) $n(\boldsymbol{r},t)$ approaches two different values n_1 and n_2, which are the stationary states of the dynamic W (i.e. $W(n_1)=W(n_2)=0$). Furthermore, let us assume that for times $t<0$ the evolution of our system is described by a travelling front solution n_0 of equation (3).

It is convenient to describe n_0 in the reference system, which moves together with the front by introducing the new variable $y=r_1-vt-r_{10}$ where v is the front velocity and r_{10} is the position of the front centre for $t=0$.

If the external noise, which perturbs the front motion, can be regarded as small we can apply the small noise expansion (Gardiner 1983) to solve equation (4). The solution can be written as the sum of n_0 and of an additional small, noise-dependent term $\tilde{n}_1(\boldsymbol{r},t)$:

$$n(\boldsymbol{r},t)=n_0(y)+\varepsilon^{1/2}\tilde{n}_1(\boldsymbol{r},t). \tag{5}$$

Substituting equation (5) in equation (4) and then selecting the terms with the same power of ε we obtain

$$D\frac{\mathrm{d}^2 n_0}{\mathrm{d}y^2}+v\frac{\mathrm{d}n_0}{\mathrm{d}y}+W(n_0)=0 \tag{6}$$

which is just another form of equation (3) and another equation which gives the time evolution of the stochastic contribution to $n(\boldsymbol{r},t)$:

$$\frac{\partial\tilde{n}_1}{\partial t}=\left[\left(\frac{\delta W}{\delta n}\right)_{n=n_0}+D\nabla^2\right]\tilde{n}_1+G(n_0)\eta(\boldsymbol{r},t). \tag{7}$$

An equation similar to (7) but with a slightly different noise term was considered by Mikhailev *et al* (1983). They assumed that the strength of noise G is given by a functional derivative of dynamics W over the parameters, which fluctuate. In such an approach many different sources of noise were introduced. As we show below, the small noise expansion can be easily performed without specifying a particular source of noise. The generalization of equation (7) to a form which takes many stochastic terms with different kinds of noises into account is also simple and straightforward.

It is convenient to use the variable y instead of x_1 in the perturbation term so we replace $\tilde{n}_1(\boldsymbol{r},t)$ by function n_1 which is defined as

$$n_1(y,r_1,\ldots,r_N,t)=n_1(r_1-vt-r_{10},\ldots,r_N,t)=\tilde{n}_1(\boldsymbol{r},t). \tag{8}$$

The equation for function n_1, which corresponds to equation (7), reads:

$$\frac{\partial n_1}{\partial t}=\left[\left(\frac{\delta W}{\delta n}\right)_{n=n_0}+D\nabla^2+v\frac{\partial}{\partial y}\right]n_1+G(n_0)\eta(y+vt+r_{10},\ldots,r_N,t). \tag{9}$$

It can be easily solved if we know the spectrum of the operator

$$\Gamma=D\sum_{j=2}^{N}\frac{\partial^2}{\partial r_j^2}+D\frac{\partial^2}{\partial y^2}+v\frac{\partial}{\partial y}+\left(\frac{\delta W}{\delta n}\right)_{n=n_0(y)}. \tag{10}$$

Let us note that eigenvectors of Γ are of the form $\exp(-\mathrm{i}\,\Sigma_{j=2}^{N} q_j r_j)\phi_\gamma(y)$, where $\phi_\gamma(y)$ is an eigenvector of the operator

$$\Gamma_1 = D\frac{\partial^2}{\partial y^2} + v\frac{\partial}{\partial y} + \left(\frac{\delta W}{\delta n}\right)_{n=n_0(y)}. \tag{11}$$

Γ_1 describes the time evolution of a small perturbation of the deterministic solution n_0 along the direction of front propagation. If n_0 is stable with respect to all perturbations, then any perturbation is damped and the spectrum of Γ_1 is non-positive. On the other hand, if n_0 is an unstable solution of the wave equation then the positive eigenvalues may exist. Γ_1 is not Hermitian (except in the case $v=0$); however, its spectrum is related to the spectrum of the Hermitian operator

$$\Gamma_{1\mathrm{H}} := D\frac{\partial^2}{\partial y^2} + \left(\frac{\delta W}{\delta n}\right)_{n=n_0(y)}. \tag{12}$$

If ν and $\psi_\nu(y)$ are eigenvector and eigenfunction of Γ_{1H} then $\gamma = \nu - v^2/4D$ and $\phi_\gamma(y) = \exp(-vy/2\mathrm{D})\psi_\nu(y)$ are eigenvalue and eigenvector of Γ_1. It is important that $\{\psi_\nu(y)\}$ form an orthogonal and complete set of vectors in the domain of $\Gamma_{1\mathrm{H}}$. Equation (9) can be easily solved if n_1 is decomposed in the basis $\{\psi_\nu(y)\}$. Let us note that

$$\begin{aligned}
&\frac{\partial}{\partial t}\left\langle \exp\left(\mathrm{i}\sum_{j=2}^{N} q_j r_j + \frac{vy}{D}\right)\phi_\gamma(y)\middle| n_1\right\rangle \\
&\qquad = \left(-D\sum_{j=2}^{N} q_j^2 + \gamma\right)\left\langle \exp\left(\mathrm{i}\sum_{j=2}^{N} q_j r_j + \frac{vy}{D}\right)\phi_\gamma(y)\middle| n_1\right\rangle \\
&\qquad\quad + \left\langle \exp\left(\mathrm{i}\sum_{j=2}^{N} q_j r_j + \frac{vy}{D}\right)\phi_\gamma(y)\middle| G(n_0)\eta(y+vt+r_{10},\ldots,r_N,t)\right\rangle_t.
\end{aligned} \tag{13}$$

Equation (13) is a linear stochastic differential equation and its formal solution reads:

$$\begin{aligned}
&\left\langle \exp\left(\mathrm{i}\sum_{j=2}^{N} q_j r_j + \frac{vy}{D}\right)\phi_\gamma(y)\middle| n_1\right\rangle(t) \\
&\qquad = \exp\left(\left(-D\sum_{j=2}^{N} q_j^2 + \gamma\right)t\right)\left\langle \exp\left(\mathrm{i}\sum_{j=2}^{N} q_j r_j + \frac{vy}{D}\right)\phi_\gamma(y)\middle| n_1\right\rangle(t=0) \\
&\qquad\quad + \int_0^t \mathrm{d}s\, \exp\left(\left(-D\sum_{j=2}^{N} q_j^2 + \gamma\right)(t-s)\right) \\
&\qquad\quad \times\left\langle \exp\left(\mathrm{i}\sum_{j=2}^{N} q_j r_j + \frac{vy}{D}\right)\phi_\gamma(y)\middle| G(n_0)\eta(y+vt+r_{10},\ldots,r_N,s)\right\rangle.
\end{aligned} \tag{14}$$

Solution (14) can be written for any noise if the stochastic integral over time can be properly defined. Let us note that it is exponentially divergent if $-D\,\Sigma_{j=2}^{N} q_j^2 + \gamma > 0$. By expanding the function $\exp(vy/2D)^* n_1(y)$ on the basis $\psi_\nu(y)\exp(\mathrm{i}\,\Sigma_{j=2}^{N} q_j r_j)$ we obtain the following expression for $n_1(\boldsymbol{r}, t)$:

$$\begin{aligned}
&n_1(y, r_2, \ldots, r_N, t) \\
&\qquad = \sum_\gamma \int \frac{\mathrm{d}q_2 \ldots \mathrm{d}q_N}{(2\pi)^{(N-1)/2}} \\
&\qquad\quad \times \exp\left(-\mathrm{i}\sum_{j=2}^{N} q_j r_j\right)\phi_\gamma(y)\left\langle \exp\left(\mathrm{i}\sum_{j=2}^{N} q_j r_j + \frac{vy}{D}\right)\phi_\gamma(y)\middle| n_1\right\rangle(t) \\
&\qquad\quad \times \left\langle \exp\left(\frac{vy}{D}\right)\phi_\gamma(y)\middle| \exp\left(\frac{vy}{D}\right)\phi_\gamma(y)\right\rangle
\end{aligned} \tag{15}$$

where the summation over γ covers all the spectrum of Γ_1. By substituting equation (14) in equation (15) we arrive at the expression for n_1 as a function of time.

However formula (14) is valid for a particular realization of the noise $\eta(\boldsymbol{r}, t)$. The quantities which are averaged over all values of the stochastic term (this average is denoted as $\langle\!\langle \ldots \rangle\!\rangle$) are more interesting, as they describe the observed behaviour of the system. Let us introduce the concentration correlation function $S(\boldsymbol{r}, \boldsymbol{z}, t)$ defined as (Gardiner 1983)

$$S(\boldsymbol{r}, \boldsymbol{z}, t) = \langle\!\langle n(\boldsymbol{r}, t) n(\boldsymbol{z}, t) \rangle\!\rangle - \langle\!\langle n(\boldsymbol{r}, t) \rangle\!\rangle \langle\!\langle n(\boldsymbol{z}, t) \rangle\!\rangle. \tag{16}$$

In the case of a travelling front it seems more appropriate to describe correlations in the system of reference, which moves together with the front. If the initial conditions at the time $t = 0$ (i.e. when the external noise appears) are the same, then the concentration correlation function is given by the following expression:

$$\begin{aligned}
&S(y_r, r_2, \ldots, r_N, y_z, z_2, \ldots, z_N, t)\\
&\quad= \langle\!\langle n(y_r + vt + r_{10}, r_2, \ldots, r_N, t) n(y_z + vt + r_{10}, z_2, \ldots, z_N, t) \rangle\!\rangle\\
&\qquad - \langle\!\langle n(y_r + vt + r_{10}, r_2, \ldots, r_N, t) \rangle\!\rangle \langle\!\langle n(y_z + vt + r_{10}, z_2, \ldots, z_N, t) \rangle\!\rangle\\
&\quad= \varepsilon \int_0^t \mathrm{d}s \int_0^t \mathrm{d}s_1 \sum_\gamma \sum_{\gamma_1} \int \frac{\mathrm{d}q_2 \ldots \mathrm{d}q_N}{(2\pi)^{(N-1)/2}} \frac{\mathrm{d}p_2 \ldots \mathrm{d}p_N}{(2\pi)^{(N-1)/2}}\\
&\qquad \times \exp\left(-\mathrm{i} \sum_{j=2}^N q_j r_j\right) \exp\left(-\mathrm{i} \sum_{j=2}^N p_j z_j\right) \phi_\gamma(y_r) \phi_{\gamma_1}(y_z)\\
&\qquad \times \exp\left(\left(-D \sum_{j=2}^N q_j^2 + \gamma\right)(t-s)\right) \exp\left(\left(-D \sum_{j=2}^N p_j^2 + \gamma_1\right)(t-s_1)\right)\\
&\qquad \times \Bigg(\int \mathrm{d}y_a \, \mathrm{d}a_2 \ldots \mathrm{d}a_N \, \mathrm{d}y_b \, \mathrm{d}b_2 \ldots \mathrm{d}b_N\\
&\qquad \times \exp\left(\mathrm{i} \sum_{j=2}^N q_j a_j + \frac{v y_a}{D}\right) \phi_\gamma(y_a) G(n_0(y_a)) \Bigg)\\
&\qquad \times \exp\left(\mathrm{i} \sum_{j=2}^N p_j b_j + \frac{v y_b}{D}\right) \phi_{\gamma_1}(y_b) G(n_0(y_b)))\\
&\qquad \times \langle\!\langle \eta(y_a + vt + r_{10}, a_2, \ldots, a_N, s) \eta(y_b + vt + r_{10}, b_2, \ldots, b_N, s_1) \rangle\!\rangle\\
&\qquad \times \Bigg[\left\langle \exp\left(\frac{vy}{D}\right) \phi_\gamma(y) \middle| \exp\left(\frac{vy}{D}\right) \phi_\gamma(y) \right\rangle\\
&\qquad \times \left\langle \exp\left(\frac{vy}{D}\right) \phi_{\gamma_1}(y) \middle| \exp\left(\frac{vy}{D}\right) \phi_{\gamma_1}(y) \right\rangle \Bigg]^{-1}.
\end{aligned} \tag{17}$$

Up to this moment we have not assumed any particular features of the noise η except the existence of the stochastic integral in equation (14), and formula (17) although quite complicated is very general. It may be simplified if the statistical properties of η are known. Let us assume that the average value of the noise $\langle\!\langle \eta(\boldsymbol{r}, t) \rangle\!\rangle = 0$ and that its correlations at different points of the system are described by the functions which depend on the distance between these points only:

$$\langle\!\langle \eta(\boldsymbol{r}, t) \eta(\boldsymbol{r}', t') \rangle\!\rangle = C_r(\boldsymbol{r} - \boldsymbol{r}') C_t(t - t'). \tag{18}$$

Condition (18) means that the system is homogeneous with respect to the noise, and the different influence of the noise on the dynamic of chemical processes comes from the concentration-dependent term $G(n_0(\boldsymbol{r}))$. The condition (18), although it allows for a separation of integration over time and space variables in equation (17), does not lead to a significant simplification. However, if the noise correlation function factorizes into the following product of contributions corresponding to different directions in space (for example, the correlations described by $\exp(-\boldsymbol{r}^2/\gamma)$ considered by Schimansky-Geier *et al* (1983) and by Malchow and Schimansky-Geier (1985) belong to this class):

$$\langle\!\langle \eta(\boldsymbol{r}, t)\eta(\boldsymbol{r}', t')\rangle\!\rangle = C_t(t-t')\prod_{j=1}^{N} C_{rj}(r_j - r_j') \tag{19}$$

then the concentration correlation function can be transformed to a quite simple form:

$$\begin{aligned} &S(y_r, r_2, \ldots, r_N, y_z, z_2, \ldots, z_N, t) \\ &\quad= \varepsilon \int_0^t \mathrm{d}s \int_{-s}^{t-s} \mathrm{d}\tau\, C_t(\tau) \sum_\gamma \sum_{\gamma_1} \exp((t-s)(\gamma+\gamma_1) - \gamma\tau) \\ &\quad\times [\pi/(D(2t-2s-\tau))]^{(N-1)/2} \\ &\quad\times \prod_{j=2}^{N} \left[\int \mathrm{d}a_j\, C_{rj}(a_j) \exp\left(-\frac{(r_j - z_j - a_j)^2}{4D(2t-2s-\tau)} \right) \phi_\phi(y_r)\gamma_{\gamma_1}(y_z) \right] \\ &\quad\times \int \mathrm{d}a_1\, \mathrm{d}b_1 \exp\left(\frac{v(y_a + y_b)}{D} \right) \phi_\gamma(y_a) G(n_0(y_a)) \phi_\gamma(y_b) \\ &\quad\times G(n_0(y_b)) C_{r1}(a_1 - b_1) \\ &\quad\times \left[\left\langle \exp\left(\frac{vy}{D}\right)\phi_\gamma(y) \middle| \exp\left(\frac{vy}{D}\right)\phi_\gamma(y) \right\rangle \right. \\ &\quad\times \left. \left\langle \exp\left(\frac{vy}{D}\right)\phi_{\gamma_1}(y) \middle| \exp\left(\frac{vy}{D}\right)\phi_{\gamma_1}(y) \right\rangle \right]^{-1}. \end{aligned} \tag{20}$$

For the white noise formula for the correlation function is very compact and it reads:

$$\begin{aligned} S(\boldsymbol{r}, \boldsymbol{z}, t) &= \varepsilon \int_0^t \mathrm{d}s \sum_\gamma \sum_{\gamma_1} \exp((\gamma+\gamma_1)(t-s)) \\ &\quad\times \exp\left(-\frac{\sum_{j=2}^{N} (r_j - z_j)^2}{8D(t-s)} \right) \frac{\phi_\gamma(y_r)\phi_{\gamma_1}(y_z)}{(4D(t-s))^{(N-1)/2}} \\ &\quad\times \frac{\int \mathrm{d}y \exp(2vy/D)\phi_\gamma(y)\phi_{\gamma_1}(y) G^2(n_0(y))}{\int \mathrm{d}y \exp(vy/D)\phi_\gamma^2(y) \int \mathrm{d}y \exp(vy/D)\phi_{\gamma_1}^2(y)}. \end{aligned} \tag{21}$$

In equations (17), (19) and (21) the summation is performed over the whole spectrum of Γ_1. It is easy to prove (by differentiation of equation (9) with respect to y) that zero is always an eigenvalue of Γ_1 and the corresponding eigenvector is $\phi_0 = \mathrm{d}n_0/\mathrm{d}y$. This solution is well known in the literature and it is called the 'Goldstone mode' (see for example Schlogl *et al* 1983). The damping factor $\exp(-\gamma s)$ is directly connected with the eigenvalue γ. Therefore the contribution from two Goldstone modes is not damped at all. The lack of front stability with respect to translations (the derivative $\mathrm{d}/\mathrm{d}y$ is a generator of the translation operator along the front propagation) can be easily understood. The boundary conditions for the front are given only at infinity and there is no mechanism which stabilizes the position of the front's centre. The physical sense of the Goldstone mode can be seen more directly if we apply the alternative description of the influence of noise on a chemical front by introducing a random function $\mathfrak{C}$ such that

$$n(\boldsymbol{r}, t) = n_0(y_r + \mathfrak{C}(\boldsymbol{r}, t)). \tag{22}$$

Assuming that the noise is small we may believe that $\mathfrak{C}(\boldsymbol{r}, t)$ is also small and therefore

$$n(\boldsymbol{r}, t) = n_0(y_r) + \phi_0(y_r)\mathfrak{C}(\boldsymbol{r}, t). \tag{23}$$

By comparing equation (22) with equation (5) one can see that

$$\mathfrak{C}(\boldsymbol{r}, t) = \tilde{n}_1(\boldsymbol{r}, t)/\phi_0(y_r). \tag{24}$$

The dispersion of $\mathfrak{C}(\boldsymbol{r}, t)$ gives us the measure of the dissipation of the front position:

$$\begin{aligned}\langle\!\langle(\delta\mathfrak{C}(\boldsymbol{r}, t))^2\rangle\!\rangle \\ &= S(\boldsymbol{r}, \boldsymbol{r}, t)\phi_0^{-2}(y_r) \\ &= \varepsilon \int_0^t \mathrm{d}s \sum_\gamma \sum_{\gamma_1} \exp((\gamma+\gamma_1)(t-s)) \frac{\phi_\gamma(y_r)\phi_{\gamma_1}(y_r)\phi_0^{-2}(y_r)}{(4D(t-s))^{(N-1)/2}} \\ &\quad \times \frac{\int \mathrm{d}y \exp(2vy/D)\phi_\gamma(y)\phi_{\gamma_1}(y)G^2(n_0(y))}{\int \mathrm{d}y \exp(vy/D)\phi_\gamma^2(y) \int \mathrm{d}y \exp(vy/D)\phi_{\gamma_1}^2(y)}.\end{aligned} \tag{25}$$

For the 1D case and when $\gamma = 0$ is separated from the rest of the spectrum of $\Gamma_{1\mathrm{H}}$ the contribution to $S(\boldsymbol{r}, \boldsymbol{r}, t)$ which comes from two Goldstone modes is the only one which is proportional to time and then the proportionality constant reads:

$$\mathfrak{D} = \varepsilon \frac{\int \mathrm{d}y \exp(2vy/D)\phi_0^2(y)G^2(n_0(y))}{(\int \mathrm{d}y \exp(vy/D)\phi_0^2(y))^2}. \tag{26}$$

$\mathfrak{D}$ can be interpreted as a 'diffusion' for spreading out the front from its deterministic position. It is interesting to note that $\mathfrak{D}$ does not depend on $\boldsymbol{r}$ or time. However, such nice behaviour of $\mathfrak{D}$ is correct only in one dimension. If $N = 2$ the contribution of the Goldstone modes is proportional to $t^{1/2}$, whereas for the higher dimensions the term $(t-s)^{-(N-1)/2}$ makes the integral in formula (25) divergent.

3. The influence of noise for front propagation for quadratic and cube dynamics

In this section we consider the noise-induced correlation function for two typical examples of chemical waves: the trigger wave which occurs between stable and metastable states and the wave which appears between the stable and unstable states. Our discussion is restricted to the 1D case; however, its generalization is easy and straightforward.

Let us start with the trigger case (the dynamic $W(n)$ is given by (1)) in which two stable states of the system are separated by the unstable state. The solution of equation (3) which at infinity approaches the different stable states is well known in the literature (Montroll 1972) and the velocity of the appearing front is equal to

$$v = (a + c - 2b). \tag{27}$$

For the numerical example let us consider the simplest case where the stable states are symmetric with respect to the unstable one and therefore $v=0$. By a suitable rescaling of variables (Magyari 1982) we can use

$$m_1 = 1-(1-\kappa)^{1/2} \qquad m_3 = 1+(1+\kappa)^{1/2}$$

and of course $m_2 = 1$. The solution n_0 reads:

$$n_0(y) = 1+(1-\kappa)^{1/2}\tanh(((1-\kappa)/2)^{1/2}y). \tag{28}$$

The spectrum of Γ_{1H} is also known (Magyari 1982). The Goldstone mode: $\phi_0 = \operatorname{sech}^2(((1-\kappa)/2)^{1/2}y)$ corresponds to $\gamma=0$. There exists the second localized mode for which eigenvalue equals: $\gamma_1 = -\frac{3}{2}(1-\kappa)$ and the eigenvector is

$$\phi_1 = \sinh(((1-\kappa)/2)^{1/2}y)\operatorname{sech}^2(((1-\kappa)/2)^{1/2}y).$$

The spectrum below $-2(1-\kappa)$ is continuous.

It is worthwhile adding that the properties of the spectrum of Γ_{1H} strongly depend on the relative positions of the stable states with respect to the unstable one (Schlogl *et al* 1983). For a large front velocity the second discrete state ϕ_1 may be found inside the continuous spectrum.

Figures 1 and 2 show the contributions to the correlation function from the discrete modes. In the numerical results presented it is assumed that $G\equiv 1$. As may be expected, the term from ϕ_1 rapidly saturates and the contribution from the Goldstone mode dominates. Therefore, if the Goldstone mode is separated from the rest of spectrum, the approximation, which takes into account the contribution from ϕ_0 only, seems reasonable for large times. On the other hand, at short times the contribution from the other eigenvectors may be dominant, because the weight of contribution depends on the scalar product with G. This effect is shown in figure 2.

Now let us consider a quadratic dynamic (equation (2)). The most interesting is the case in which two stationary states of $W(n)$ exist. Let us denote these states by m_1 and m_2 ($m_1 < m_2$). Now dynamics (2) can be written as

$$W(n) = -\gamma(n-m_1)(n-m_2). \tag{29}$$

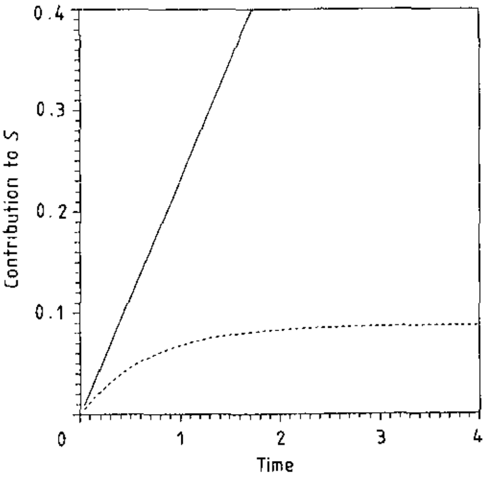

Figure 1. The contributions to the correlation function: $S(r=1, r=1, \gamma=0, \gamma_1=0, t)$ (the full line) and $S(r=1, r=1, \gamma=-3(1-\kappa)/2, \gamma_1=-3(1-\kappa)/2, t)$ (the dashed curve) for a trigger wave ($\kappa=0.5$) plotted as a function of time.

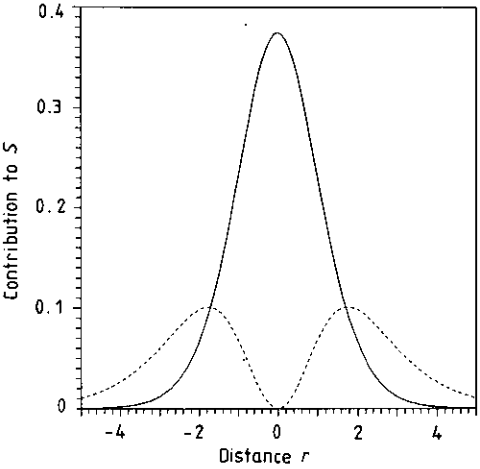

Figure 2. The contributions to the correlation function: $S(r, r, \gamma=0, \gamma_1=0, t=1)$ (the full curve) and $S(r, r, \gamma=-3(1-\kappa)/2, \gamma_1=-3(1-\kappa)/2, t=1)$ (the dashed curve) for a trigger wave ($\kappa=0.5$) plotted as a function of r.

In equation (29) γ has to be positive, because it is associated with the rate of recombination. Therefore m_1 is an unstable stationary state and m_2 is a stable one. For dynamics (29) the corresponding stochastic reaction diffusion equation (equation (4)) reads:

$$\frac{\partial n}{\partial t}=-\gamma(n-m_1)(n-m_2)+D\nabla^2 n+\varepsilon^{1/2}G(n)\eta(\boldsymbol{r}, t). \tag{30}$$

By simple scaling of the variables one can transform equation (30) to a much simpler form. Introducing the reduced concentration

$$n':=(n-m_1)/m_{12} \tag{31}$$

where $m_{12}=m_2-m_1$ and new time and position variables

$$t'=t(m_{12}\gamma) \tag{32}$$

$$x'=x(m_{12}\gamma/D)^{1/2} \tag{33}$$

one arrives at the standard form of the evolution equation:

$$\frac{\partial n'}{\partial t'}=-n'(n'-1)+\nabla^2 n'+\frac{\varepsilon^{1/2}}{\gamma m_{12}^2}G(m_{12}n'+m_1)\eta(\boldsymbol{r}, t). \tag{34}$$

In this coefficient-free form of stochastic reaction-diffusion equation the strength of the external noise scales by the factor $(\gamma m_{12}^2)^{-1}$. In the following, we restrict our discussion to equation (34); however, having in mind the transformations (31)-(33) one can always return to the original variables.

Let us consider the case in which $n(x_1)\rightarrow m_2$ $(n'\rightarrow 1)$ for $x_1\rightarrow -\infty$ and $n(x_1)\rightarrow m_1$ $(n'\rightarrow 0)$ for $x_1\rightarrow\infty$. As both the limiting values of concentration are stationary in time we may expect that transition from the unstable to the stable stationary state may be observed as a travelling front of concentration. The profile n' of a front which moves with the velocity v' in a system without the external noise ($\varepsilon = 0$) is described by the equation

$$\frac{d^2 n'_0}{dy^2} + v' \frac{dn'_0}{dy} - n'_0(n'_0 - 1) = 0. \tag{35}$$

The scaled v and the original one v' front velocities are related by the factor $(Dm_{12}\gamma)^{1/2}$ ($v = v'(Dm_{12}\gamma)^{1/2}$).

The dynamic (2), unlike the third-order chemical dynamics (1), admits many solutions with different velocities. This can be clearly seen by invoking the following mechanical analogy. If we replace the space variable y by time and the concentration by position, then we find that equation (35) transforms to an equation of motion for a particle with a unit mass in a medium in which friction is proportional to velocity. A chemical dynamics represents a force. In such an approach the value of the front's velocity becomes the friction coefficient. A chemical front between a stable and unstable state corresponds to a particle situated at the beginning close to $x = 0$ which moves towards $x = 1$. If the friction coefficient is small then the particle will first cross $x = 1$ and then return to this point. For large friction coefficients (i.e. large velocities of a front) the motion is strongly damped and there is no overshooting. This example shows us that there exists a minimal front velocity for which the values of concentration are limited to the interval $[m_1, m_2]$. Of course the values of concentration remain inside this range for the fronts with velocity higher than the critical one.

It is also easy to prove that the fronts with velocity larger than a critical value are stable with respect to small *local* perturbations. Let us consider a solution of equation (35): $n_0(y)$, for which velocity equals v', and let us assume that its perturbation $g(y, t)$ can be written in the form

$$g(y, t) = h(y) \exp(-v'y/2 + \gamma t') \tag{36}$$

by substituting (36) in (9) one finds that the function h should satisfy the equation

$$\frac{d^2 h}{dy^2} - (v'^2/4 + 2n_0 - 1)h = \gamma h. \tag{37}$$

If $v' > v'^* = 2$ then the term $v'^2/4 + 2n_0 - 1$ is never negative because $n_0 \geqslant 0$. Therefore the eigenvalue γ cannot be positive. It shows that, within the linear analysis of stability, all the fronts with velocity not smaller than 2 are stable with respect to the local perturbations. The velocity $v'^* = 2$ is the minimal one, for which such stability appears. It has been proved by Aronson and Weinberger (1978) that this velocity is the one which actually appears in the systems with quadratic dynamics.

The application of small noise expansion simplifies if an analytical solution of equation (35) is known. For the quadratic dynamics the analytical form of solution corresponding to v'^* is not known, but there exists a solution for velocity only slightly exceeding v'^* (Kaliappan 1984).

Let us assume that there exists a solution $n(y)$ of equation (35) for which the derivative can be expressed in the following form:

$$\frac{dn}{dy} = \sigma_1 n^{\omega_1} + \sigma_2 n^{\omega_2}. \tag{38}$$

This, quite peculiar, assumption allows us to transform equation (35) into an algebraic form. A straightforward calculation shows that condition (38) holds if: $\omega_1 = 1$, $\omega_2 = \frac{3}{2}$,

$\sigma_1 = -(\frac{2}{3})^{1/2}$ and $\sigma_2 = (\frac{2}{3})^{1/2}$. The solution for the front's profile is

$$n_0'(y') = (1 + \Lambda \exp(y'/\sqrt{6}))^{-2} \tag{39}$$

and the corresponding velocity equals (Kaliappan 1984) $v' = 5/\sqrt{6} = v'^{*}(\frac{25}{24})^{1/2}$ (or in the original variables $v = 5\ (Dm_{12}\gamma/\sqrt{6})^{1/2}$). The constant Λ in equation (39) depends only on the initial conditions. We may put $\Lambda = 1$ by choosing the reference system, in which $n(y = 0) = 0.5$.

The solution (39), for which velocity is very close to the critical one, seems to be useful as a basis for an application of the small noise expansion and for studying the influence of external fluctuations on the front's motion. To calculate the correlation function S we should know the spectrum of the operator Γ_1 (equation (11)), so the following equation has to be solved:

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}y^2} + v'\frac{\mathrm{d}}{\mathrm{d}y} + 1 - 2n_0'(y)\right]\phi_\gamma = \gamma\phi_\gamma. \tag{40}$$

To estimate the range of γ in which the continuous spectrum may appear, we perform the analysis similar to that presented by Schlogl *et al* (1983) for the trigger wave. Let us consider the following asymptotic ($y \to \pm\infty$) form of solution of equation (40):

$$\phi_\gamma(y) = \exp(-v'y/2)(A_\pm \exp(\kappa_\pm y) + B_\pm \exp(-\kappa_\pm y)) \tag{41}$$

where + and − signs correspond to $y \to +\infty$ and $y \to -\infty$. Substituting equation (41) in equation (40) and taking the boundary conditions for n_0' into account, we obtain the expressions for κ_+ and κ_-:

$$\kappa_+ = (\gamma + \tfrac{1}{24})^{1/2} \tag{42}$$

and

$$\kappa_- = (\gamma + \tfrac{49}{24})^{1/2}. \tag{43}$$

First let us note that B_- has to be equal to zero because otherwise ϕ_γ is divergent in the limit $y \to -\infty$. To ensure the convergence of the first term of (41) $-v'/2 + \kappa_-$ have to be non-negative so that $\gamma \geqslant -1$.

In the limit $y \to +\infty$ the asymptotic form (41) gives the damped oscillations of ϕ_γ for $\gamma < -\frac{1}{24}$. If $\gamma \in [-\frac{1}{24}, 1]$ then the functions ϕ_γ are uniformly damped.

The second term of the product in equation (41): $(A_\pm \exp(\kappa_\pm y) + B_\pm \exp(-\kappa_\pm y))$ is of course a solution of equation (37), which is isomorphic with the Schrödinger equation for the potential $2n_0 + v'^2/4 - 1$. The eigenvalue corresponds to the total energy. The oscillating solutions of equation (40) describe asymptotically ($y \to +\infty$) free solutions of the Schrödinger equation; the energy of such solutions exceeds $v'^2/4 - 1 = \frac{1}{24}$. Let us also observe that if we use the wave profile corresponding to the minimal stable velocity, rather than n_0', then the potential vanishes at infinity and the spectrum of oscillating solutions starts at $\gamma = 0^-$ and it is not separated from the Goldstone mode.

The eigenvectors with $\gamma < 0$ are damped in time. The contributions from the positive eigenvalues are more important in formulae for the correlation function and the related quantities because these contributions lead to divergent terms. If such contributions exist the use of the small noise expansion is not justified.

By introducing the new variable $z := (1 + \tanh(y/2\sqrt{6}))/2$ one can transform equation (40) into the form

$$\left(z^2(1-z)^2\frac{\mathrm{d}^2}{\mathrm{d}z^2} + 2z(1-z)(3-z)\frac{\mathrm{d}}{\mathrm{d}z} - 12(1-z)^2 + 6(1+\gamma)\right)\phi_\gamma = 0. \tag{44}$$

Equation (44) can be transformed into the hypergeometric form if the following form of solution is assumed:

$$\phi_\gamma(z)=(1-z)^q z^p \psi_\gamma(z) \tag{45}$$

where

$$q^2-5q+6(1-\gamma)=0$$

and

$$p^2+5p-6(1+\gamma)=0.$$

ψ_γ defined by equation (45) should satisfy

$$z(1-z)\psi''_\gamma+[2(3+p)-(p+q+4)(p+q-3)z]\psi'_\gamma+(p+q+4)(p+q-3)\psi_\gamma=0. \tag{46}$$

Using the textbook solution of equation (46) one can write the following formula for ϕ_γ:

$$\begin{aligned}\phi_\gamma(z)=A_1&(1-z)^q z^p F(p+q-3,p+q+4,2(3+p),z)\\ &+A_2(1-z)^q z^{-5-p} F(q-2p-8,p-2q-1,-4-2q,z)\end{aligned} \tag{47}$$

where F denotes the hypergeometric function. For a regular solution both the powers at z and $1-z$ must be non-negative. If a solution in the form (47) is supposed to be bounded its parameters q and p have to satisfy one of the conditions

$$p+q-3=-l \tag{48}$$

or

$$q-2p-8=-l \tag{49}$$

where $l\in\mathbb{N}$. It is easy to note that there are no bounded solutions corresponding to (49). If q and $-p-5$ are to be non-negative then of course $q-2p-8$ must be positive. On the other hand we can easily find two solutions, which satsfy (48). For $l=0$ we have

$$p=1,\ q=2\ (\gamma=0) \qquad \text{and} \qquad \psi_0\equiv 1 \text{ (the Goldstone mode)}$$

and for $l=1$ the solution reads

$$p=1.5 \qquad q=0.5\ (\gamma=\tfrac{5}{8}) \qquad \text{and} \qquad \psi_{5/8}=3-2z.$$

Each of these solutions given above, if written in the form (36), leads to a function h which is exponentially divergent for $y\to+\infty$. Therefore these functions do not belong to the set of solutions of equation (37). The corresponding function $g(y,t)$ is not local; it extends over the whole space.

Let us observe that the second solution describes a perturbation of n'_0 which is exponentially divergent in time. It shows that the special analytical solution (39) is not stable against non-local perturbations and it cannot be used as a basis for the small noise expansion. On the other hand, if the solution corresponding to v'^* is used in the small noise expansion then the Goldstone mode is not separated from the continuous spectrum. In this case the expression for the correlation function should contain the summation over the spectrum around $\gamma=0$. Therefore the method in which the contribution to the front propagation from the Goldstone mode is separated from the others and it is assumed to be dominant (Mikhailev *et al* (1983), Schimansky-Geier *et al* (1983)) cannot be applied to systems with quadratic chemical dynamics.

4. Conclusions

The reaction–diffusion equation, supplemented by a stochastic term, may be applied to describe the time evolution of a chemical system under the influence of the external noise. However, such an approach usually leads to complicated stochastic differential equations, which are very difficult to solve. The small noise expansion seems to be a useful approximation which enables one to write such an equation in a linear form, so that the standard methods of solution for linear stochastic equations can be easily applied and further calculations of relevant quantities possible (here the correlation function for concentration). We are aware that the actual meaning and validity of this expansion are not trivial (Gardiner 1983). The sensibility of the expansion depends critically on the form of the chemical dynamics and on the character of the initial state. Generally speaking, the small noise expansion seems to be justified if the dynamics W and the initial state of the system ensure convergence to a single stable state.

In this paper we discussed the application of the small noise expansion for the description of the correlations, which may appear around a randomly perturbed chemical front. The results presented above generalize those obtained by Mikhailev *et al* (1983) and by Schimansky-Geier *et al* (1983) because they are not restricted to the contribution from the Goldstone mode only. The simplification used by these authors seems to be justified in the case when the Goldstone mode is separated from the continuous part of spectrum of Γ_{1H}. In this case it is possible to consider separately the perturbations of the shape and of the position of a travelling wave. We have also shown that in the case of the quadratic chemical dynamics such separation is no longer valid for the analytical solution due to Kaliappan (1984) and for $v^* = 2$.

Finally, we would like to mention that application of stochastic differential equations seems to be the most straightforward description of the stochastic correlations in a randomly perturbed chemical front. Nevertheless it is also possible to adapt the alternative formalism based on the Fokker–Planck equation (Gardiner 1983).

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