ON THE INFLUENCE OF INTERNAL FLUCTUATIONS ON AN OSCILLATING CHEMICAL SYSTEM*

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In this paper we study the influence of external fluctuations on a model oscillating chemical system. The stability of spatially homogeneous, oscillating state against local fluctuations is discussed for various space dimensions. A possibility of an oscillating state in a parameter region, where no oscillations are predicted by the phenomenological theory, is discussed.

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1. Introduction

The stability of spatially and temporally ordered behaviour of chemical systems has attracted a lot of scientific attention in the recent years [1]. Many theoretical works are concerned with the linear analysis of the effect of small time- and space- dependent fluctuation on a given pattern [2]. The phase dynamics formalism of Kuramoto [3] and Sivahinsky [4] is an example of the general approach to the problem of noise influenced spatio-temporal patterns, which avoids the drawbacks of a naive perturbation method. In the final formulation of Kuramoto [5] the effect of fluctuations is described by a Brownian motion of the interface position and a small profile perturbation which depends on time and on location on the interface.

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The present work is concerned with the influence of fluctuations on a temporally ordered evolution. Let us notice that in homogeneous phase transitions the nonlinear influence of fluctuations on the dynamics determines the stability of an ordered phase at nonvanishing temperatures at different spatial dimensionalities. The aim of this paper is to show how this problem can be approached in the case of a simple model which exhibits a temporal pattern formation. The results are pretty similar to the homogeneous phase transition case [6]. We have shown that within an approximate self-consistent model the temporal pattern is stable only in a three dimensional space. In the one- and two- dimensional case we study the decay of the initially formed temporal pattern. The nonlinear feedback of fluctuations determines a "coherence time" in which the relaxation of an initially ordered state occurs. The decay of an oscillating state which is formed in a parametric space region, where the phenomenological theory does not allow for the existence of oscillations is also studied. Its found that the amplitude of oscillations below the critical point is proportional to the strength of noise (inversely proportional to the size of the system). Such behavior has been observed in recent molecular dynamics simulations of chemical reactions [7].

2. The model and its linear stability

Let us consider a system with two chemically active reagents U and V, which concentrations (denoted as u, v) evolve according to the following stochastic reaction-diffusion equations:

$$\frac{\partial u}{\partial t} = -v + u(K - (u^2 + v^2)) + D\nabla^2 u + \xi_u \,, \tag{1}$$

$$\frac{\partial v}{\partial t} = u + v(K - (u^2 + v^2)) + D\nabla^2 v + \xi_v \,, \tag{2}$$

which are regarded as Ito stochastic differential equations. In the homogeneous case, if the noise terms are neglected, the system is characterized by a single stationary state $(v = 0, u = 0)$ for $K < 0$. For $K > 0$ this state becomes unstable and the stable limit cycle of the radius $\sqrt{K}$ appears.

We assume that white noises ξ_u, ξ_v, which are spatially and temporally dependent, have the following properties:

$$\langle \xi_u(\boldsymbol{x},t)\xi_v(\boldsymbol{x}',t')\rangle = 0 \,, \tag{3a}$$

$$\langle \xi_u(\boldsymbol{x},t)\xi_u(\boldsymbol{x}',t')\rangle = \varepsilon C(\mid \boldsymbol{x} - \boldsymbol{x}' \mid)\delta(t-t') \,, \tag{3b}$$

$$\langle \xi_v(\boldsymbol{x},t)\xi_v(\boldsymbol{x}',t')\rangle = \varepsilon C(\mid \boldsymbol{x} - \boldsymbol{x}' \mid)\delta(t-t') \,. \tag{3c}$$

Eq. (3a) means that these noises are uncorrelated and Eqs. (3b, 3c) say that they influence the dynamics of both reagents with the same strength.

The function $C(|\boldsymbol{x} - \boldsymbol{x}'|)$ describes the spatial correlations of the noise in different points of space. For the detailed calculations presented below we adopt the following form of C:

$$C(|\boldsymbol{x} - \boldsymbol{x}'|) = \frac{1}{(\Lambda\sqrt{\pi})^d} \exp\left(-\frac{(\boldsymbol{x} - \boldsymbol{x}')^2}{\Lambda^2}\right), \tag{4}$$

where Λ is a constant and d denotes system's dimensionality. In the limit of $\Lambda \to 0$ Eq. (4) defines the noise which is uncorrelated in space. It comes out that the noise correlation length Λ plays the role of cutoff in the momentum space. It seems more realistic to introduce the spatial cutoff, which is always associated to reaction diffusion models, in the definition of the noise correlation function rather then in the definition of the interval over momentum space. On the other hand we assume that there are no correlations between noises at different moments of time. From the physical point of view Eqs. (1) and (2) may be regarded as an approximation of more complex chemical dynamics with respect to a small perturbation around a homogeneous, steady state [8].

Let us introduce a new complex variable:

$$z = u + iv, \tag{5a}$$

which may be represented in terms of the amplitude ρ and phase φ:

$$z = \rho \exp(i\varphi). \tag{5b}$$

Eqs. (1), (2) are equivalent to the following single equation for z

$$\frac{\partial z}{\partial t} = iz + z(K - |z|^2) + D\nabla^2 z + (\xi_u + i\xi_v), \tag{6}$$

however, it is more convenient to use ρ and φ for the definition of a temporal pattern and for the analysis of its linear stability. The evolution of these variables is described by equations:

$$\frac{\partial \rho}{\partial t} = \rho(K - \rho^2) + D\nabla^2\rho - D\rho(\nabla\varphi)^2 + \frac{\varepsilon C(0)}{2\rho} + \xi_\rho, \tag{7}$$

$$\frac{\partial \varphi}{\partial t} = 1 + \frac{2D}{\rho}\nabla\varphi\nabla\rho + D\nabla^2\varphi + \frac{\xi_\varphi}{\rho}, \tag{8}$$

where the new noises ξ_ρ and ξ_φ are obtained by the rotation of the original noises acting on u and v:

$$\xi_\rho = \xi_u \cos\varphi + \xi_v \sin\varphi, \tag{9a}$$

$$\xi_\varphi = \xi_v \cos\varphi - \xi_u \sin\varphi\,. \tag{9b}$$

It may be easily checked that the noises ξ_ρ, ξ_φ are independent and their dispersions are the same as those of the noises ξ_u, ξ_v. One may notice (Eq. (8)) that for small ρ the phase noise ξ_φ becomes important. It is understandable because if the amplitude of oscillations is small then fluctuations may randomly move the system on the limit cycle and the influence of such fluctuations on the phase φ is large. In Eq. (7) the term coming from Ito's interpretation of stochastic differential equations: $(\frac{\varepsilon C(0)}{2\rho})$ appears. This term has no mathematical meaning if the noise is uncorrelated in space $(C(\mid \boldsymbol{x} - \boldsymbol{x}' \mid) = \delta(\boldsymbol{x} - \boldsymbol{x}'))$. The presence of this term changes the amplitude of a stationary state with respect to the case when noise is neglected. The phenomenological stationary state ($\rho = 0$) disappears in the presence of noise. The radius corresponding to the stable stationary state is shifted from $\rho_{ph} = \sqrt{K}$ to the value:

$$\rho_0 = \sqrt{\frac{K}{2} + \frac{1}{2}\sqrt{(2\varepsilon C(0) + K^2)}}\,. \tag{10}$$

The solution for the average amplitude and phase of homogeneous oscillations obtained from Eq. (7) and (8) reads: $\langle\rho\rangle = \rho_0, \langle\varphi\rangle = t$. For large positive K the value of ρ_0 can be approximated by:

$$\rho_0 = \rho_{ph}\left(1 + \frac{\varepsilon C(0)}{4K^2}\right). \tag{11}$$

In this case the presence of noise increases the amplitude of limit cycle.

What is more important Eq. (10) predicts nonzero radius of oscillations below the phenomenological critical point ($K = 0$). Near the critical point if $\mid K \mid^2 \ll \varepsilon C(0)$ the amplitude of the steady state is given by:

$$\rho_0 \cong \left(\frac{\varepsilon C(0)}{2}\right)^{1/4}. \tag{12}$$

As we shall show later, this rather peculiar regime of oscillations, driven by noise, is stable in sense that the standard deviation of amplitude fluctuations may be smaller than ρ_0.

For $K \ll 0$ the amplitude may be approximated as:

$$\rho_0 \cong \sqrt{\frac{\varepsilon C(0)}{2 \mid K \mid}}\,. \tag{13}$$

It indicates that in the presence of noise oscillations may appear also below the phenomenological critical point. This phenomenon has been observed in molecular dynamics simulations of a model of oscillating reaction [7].

Now let us consider the influence of noise on the homogeneous oscillating solution of Eqs. (6), (7): $\rho = \rho_0, \varphi = t$. Let $\tilde{\rho}, \tilde{\varphi}$ denote a small, local perturbation of this solution. In the following we consider the evolution of a state, which at the beginning corresponds to a homogeneous limit circle (*i.e.* $\tilde{\rho}(t=0) = 0$ and $\tilde{\varphi}(t=0) = 0$). Within the simplest linear approximation the evolution of $\tilde{\rho}, \tilde{\varphi}$ is described by the following equations:

$$\frac{\partial \tilde{\rho}}{\partial t} = -2\tilde{\rho}\sqrt{K^2 + 2\varepsilon C(0)} + D\nabla^2\tilde{\rho} + \xi_\rho\,, \tag{14a}$$

$$\frac{\partial \tilde{\varphi}}{\partial t} = D\nabla^2\tilde{\varphi} + \frac{\xi_\varphi}{\rho_0}\,. \tag{14b}$$

Equations (14) are independent and they analytical solution can be easily written [9]. Let us assume that the system is enclosed within a d-dimensional cube with a side length L. Expressing $\tilde{\rho}$ and $\tilde{\varphi}$ by their Fourier transforms, defined as:

$$f_{\boldsymbol{k}} = \frac{1}{L^d}\int_V d^d\boldsymbol{x} f(\boldsymbol{x}) \exp(-i2\pi\boldsymbol{x}\boldsymbol{k}/L)\,,$$

where $V(= L^d)$ is the volume of the system, one obtains linear stochastic differential equations for $\tilde{\rho}$ and $\tilde{\varphi}$. In the $\boldsymbol{k}$-space the relation (3) leads to:

$$\langle \xi_\rho(\boldsymbol{k},t)\xi_\rho(\boldsymbol{k}',t')\rangle = \langle \xi_\varphi(\boldsymbol{k},t)\xi_\varphi(\boldsymbol{k}',t')\rangle = \frac{\varepsilon C_{\boldsymbol{k}}}{V}\delta_{\boldsymbol{k}+\boldsymbol{k}',0}\,\delta(t-t')\,, \tag{15}$$

and for the correlations of noise defined by Eq. (4) the function $C_{\boldsymbol{k}}$ reads:

$$C_{\boldsymbol{k}} = \exp\left(-\left(\frac{\pi \Lambda \boldsymbol{k}}{L}\right)^2\right). \tag{16}$$

It is easy to see that all the Fourier components of $\tilde{\rho}$ (including the one corresponding to $\boldsymbol{k} = 0$) are damped in time. The expression for the amplitude fluctuations comes directly from solution of Eq. (14). In the limit $t \to \infty$ it reads:

$$\langle \tilde{\rho}^2(x)\rangle = \frac{\varepsilon}{2V}\sum_{\boldsymbol{k}} \frac{C_{\boldsymbol{k}}}{D(2\pi\boldsymbol{k}/L)^2 + 2\sqrt{K^2+2\varepsilon C(0)}}\,. \tag{17}$$

In the thermodynamic limit (large L) we can replace the sum with an integral over the Fourier space:

$$\frac{1}{V}\sum_{\boldsymbol{k}\neq 0} g\left(\frac{2\pi\boldsymbol{k}}{L}\right) = \frac{1}{(2\pi)^d}\int d^d\boldsymbol{q}\, g(\boldsymbol{q})\,. \tag{18}$$

Introducing an inverse correlation length m as:

$$m^2 = 2\sqrt{K^2 + 2\varepsilon C(0)}\,, \tag{19}$$

and using C_k given by Eq. ((16) we obtain:

$$\langle \tilde{\rho}^2 \rangle = \frac{\varepsilon}{2} m^{d-2} f\left(\frac{\Lambda m}{2}\right), \tag{20}$$

where

$$f(x) = \frac{1}{(2\pi)^d} \int d^d \boldsymbol{q} \frac{1}{Dq^2 + 1} \exp(-(qx)^2)\,. \tag{21}$$

In the case of large positive K

$$\frac{\sqrt{\langle \tilde{\rho}^2 \rangle}}{\rho_0} \sim \frac{\sqrt{\varepsilon}}{K \Lambda^{\frac{d}{2}}}, \tag{22}$$

and such results are in the agreement with the intuitive idea that the noise has a marginal effect on a stable cycle.

On the other hand if K is negative and $\varepsilon \ll \mid K \mid$ then

$$\frac{\sqrt{\langle \tilde{\rho}^2 \rangle}}{\rho_0} \sim \frac{1}{\sqrt{C(0)} \Lambda^{\frac{d}{2}}}, \tag{23}$$

which is always finite independently of space dimensionality and does not depend on the strength of the noise. This behavior is obviously far away from the predictions of phenomenological analysis. It the noise correlation length is large than the dispersion of $\tilde{\rho}$ may be smaller than ρ_0 and thus the noise induced oscillations should be visible.

Close to the phenomenological critical point ($\mid K \mid \ll \varepsilon$) we have:

$$\frac{\sqrt{\langle \tilde{\rho}^2 \rangle}}{\rho_0} \sim \varepsilon^{\frac{d-1}{4}}\,. \tag{24}$$

Therefore, the standard deviation of the radius goes to zero for dimensionalities $d = 2$ and 3 so oscillations may be observed.

The average behavior of the system is described by the average of the complex field z over the realizations of the noises and the initial conditions. Having in mind that the noses ξ_ρ and ξ_φ are independent and taking into account their Gaussian character, we have:

$$\langle z \rangle = \rho_0 \langle \exp i\tilde{\varphi} \rangle \exp(it) = \rho_0 \exp\left(-\tfrac{1}{2}\langle \tilde{\varphi}^2 \rangle\right) \exp(it)\,. \tag{25}$$

The solution of Eq. (14b) reads:

$$\tilde{\varphi}_{k}(t) = \exp\left(-D\left(\frac{2\pi k}{L}\right)^2 t\right) \int\limits_0^t ds \exp\left(D\left(\frac{2\pi k}{L}\right)^2 s\right) \frac{\xi_{\varphi k}(s)}{\rho_0}\,, \tag{26}$$

and

$$\langle\tilde{\varphi}^2(x)\rangle = \frac{\varepsilon C_0 t}{V\rho_0^2} + \frac{\varepsilon}{V\rho_0^2}\sum_{k\neq 0} C_k \exp\left(-2D\left(\frac{2\pi k}{L}\right)^2 t\right) \int\limits_0^t ds \exp\left(2D\left(\frac{2\pi k}{L}\right)^2 s\right). \tag{27}$$

The first term of Eq. (27) is associated with the homogeneous diffusion of the phase. It must be noted that the size of the system slows down this homogeneous diffusion. The characteristic time for this process is of the order of $\frac{V\rho_0^2}{\varepsilon}$ and defines a natural upper limit for the temporal coherence of the system. At this time scale the linearization procedure leads naturally to the Kuramoto's result, which says that a pattern under the influence of a small disturbance retains it shape, but the Goldstone modes parameters (in our case it is the phase) become a time dependent local quantities. In the following we shall be interested in the system stability for much shorter times. This stability is determined by the relaxation of local phase fluctuations associated with the second term of Eq. (27). This term depends on the dimensionality of the system. Taking into account the correlations of noise in the form given by Eq. (16) one obtains:

$$\langle\tilde{\varphi}^2(x)\rangle = \frac{\varepsilon t}{V\rho_0^2} + \frac{\varepsilon}{\rho_0^2}\frac{1}{4D\sqrt{\pi}}\left(\sqrt{8Dt+\Lambda^2} - \Lambda\right) \qquad \text{for } d=1\,, \tag{28a}$$

$$\langle\tilde{\varphi}^2(x)\rangle = \frac{\varepsilon t}{V\rho_0^2} + \frac{\varepsilon}{\rho_0^2}\frac{1}{8\pi D}\ln\left(\frac{8Dt+\Lambda^2}{\Lambda^2}\right) \qquad \text{for } d=2\,, \tag{28b}$$

$$\langle\tilde{\varphi}^2(x)\rangle = \frac{\varepsilon t}{V\rho_0^2} + \frac{\varepsilon}{\rho_0^2}\left(\frac{1}{\sqrt{\pi}}\right)^3\frac{1}{4D}\left(\frac{1}{\Lambda} - \frac{1}{\sqrt{8Dt+\Lambda^2}}\right) \qquad \text{for } d=3\,. \tag{28c}$$

For a large volume we can neglect the instability related to a homogeneous phase diffusion, which is associated with the first term of Eq. (27). Because of the second term of Eqs. (27) the nonhomogeneous phase fluctuations make the ordered state unstable in one- and two-dimensions. On the other hand, for $d = 3$ the second term in Eq. (28c) converges to the finite value. This result is in an agreement with what is expected from the analogy with equilibrium phase transitions *i.e.* correlations introduced by large dimensionality enforce a coherent behavior which should be stable if only local, uncorrelated, noise induced fluctuations are considered.

3. Fluctuations in the nonlinear regime

The main limitation of the analysis presented in the previous section is the neglecting of the feedback of phase fluctuations on the amplitude of the ordered phase given by the term $D\rho(\nabla\varphi)^2$ in Eq. (7). A simple model of fluctuations, which goes beyond the linearized theory, can be introduced by means of a suitable mean-field like approximation. Some possible approximations of this kind are discussed below.

A generalization of the phasedynamics approach in the nonlinear regime can be achieved as follows. We assume that the correlations between local fluctuations of the amplitude and phase can be always neglected. For instance, in the case of large K there is a strong restoring force, which will quickly dump out amplitude oscillations. Thus, we can assume that as far as the long time behavior of phase fluctuations is concerned the amplitude is constant as a function of space and it is slowly varying in time because of a coupling with phase fluctuations. On the other hand, nonhomogeneous phase fluctuation modify the stationary state of the amplitude. As a consequence the local phase (amplitude) fluctuations appearing in the local amplitude (phase) equation are substituted by their average values with respect to a restricted ensemble where only phase (amplitude) fluctuations are considered:

$$\frac{\partial\rho}{\partial t} = \rho(K-\rho^2) + \frac{\varepsilon C(0)}{2\rho} + D\nabla^2\rho - D\rho\langle(\nabla\varphi)^2\rangle + \xi_\rho\,, \qquad (29)$$

$$\frac{\partial\varphi}{\partial t} = 1 + D\nabla^2\varphi + \frac{2D}{\rho}\nabla\varphi\langle\nabla\rho\rangle + \frac{\xi_\varphi}{\rho}\,. \qquad (30)$$

Let us consider a stationary state characterized by a constant in space average amplitude and a phase, which may depend on a space variable. The following relationship for the amplitude of a homogeneous stationary state ρ_s comes out from Eq. (29):

$$\rho_s(K - D\langle(\nabla\varphi)^2\rangle - {\rho_s}^2) + \frac{\varepsilon C(0)}{2\rho_s} = 0\,. \qquad (31)$$

It shows that the presence of phase fluctuations decreases the stationary state amplitude. Moreover, in the case of large nonhomogeneous fluctuations ($K \leq D\langle(\nabla\varphi)\rangle^2$) the amplitude of a stationary state is reduced to the order of ε. This regime is obviously far beyond the linear approximation presented in the previous section, where the presence of fluctuations can only increase the amplitude.

Within the restricted ensemble assumption we may obtain the average over phase noise of the inhomogeneous phase fluctuations ξ_φ. Let us consider a homogeneous state of phase for $t \leq 0$ and noise, which appears for $t > 0$. In such case

$$\begin{aligned}
&\langle (\nabla\varphi)^2(t)\rangle \\
&= \frac{\varepsilon}{V\rho_s^2}\sum_{k\neq 0}\left(\frac{2\pi k}{L}\right)^2 C_k \exp\left(-2D\left(\frac{2\pi k}{L}\right)^2 t\right)\int_0^t ds \exp\left(2D\left(\frac{2\pi k}{L}\right)^2 s\right), \\
&= \frac{\varepsilon}{V\rho_s^2}\frac{1}{2D}\sum_{k\neq 0} C_k\left(1-\exp\left(-2D\left(\frac{2\pi k}{L}\right)^2 t\right)\right), \\
&= \frac{\varepsilon C(0)}{2D\rho_s^2} - \frac{\varepsilon C_0}{2DV\rho_s^2} - \frac{\varepsilon}{2DV\rho_s^2}\sum_{k\neq 0} C_k \exp\left(-2D\left(\frac{2\pi k}{L}\right)^2 t\right). \qquad (32)
\end{aligned}$$

Substituting (32) to (31) one obtains:

$$\rho_s(K-\rho_s{}^2) + \frac{\varepsilon C_0}{2V\rho_s} + \frac{\varepsilon}{2\rho_s(2\pi)^d}\int d^d q C_q \exp(-2Dq^2 t) = 0\,. \qquad (33)$$

The formal solution of Eq. (33) is in the form of (10) and reads:

$$\rho_s = \sqrt{\frac{K}{2} + \frac{1}{2}\sqrt{K^2 + 2\varepsilon\left(\frac{C_0}{V} + \frac{1}{(2\pi)^d}\int d^d q C_q \exp(-2Dq^2 t)\right)}}\,. \qquad (34)$$

In the long time limit the integral may be neglected and the stationary radius of the circle is:

$$\rho_{s,\infty} = \sqrt{\frac{K}{2} + \frac{1}{2}\sqrt{K^2 + 2\varepsilon\frac{C_0}{V}}}\,, \qquad (35)$$

which in the limit of a large volume converges to the phenomenological value ρ_{ph}. Therefore, the inclusion of phase fluctuations almost completely cancels out the effect of noise on the radius predicted by the small noise expansion.

An alternative mean-field like approach to the problem is based on the following approximations. Let us substitute the modulus of the complex process z in Eq. (6) ($| z |^2$) by its spatial average. It is worthwhile to note that this approximation is not equivalent to the substitution of the local value of modulus with the ensemble average. The difference between these two approximation schemes can be explained by the intrinsic non-ergodicity of the model. Let us show that the model we considered exhibits a quite different mechanism for long time behavior at small dimensionalities.

Within the approximations introduced one obtains equations describing the time evolution of the Fourier components. It is convenient to separate the $\boldsymbol{k} = 0$ component from the others. For $\boldsymbol{k} \neq 0$ we have:

$$\frac{\partial z_k}{\partial t} = iz_k + z_k\left(K - \mid z_0 \mid^2 - \sum_{l\neq 0} \mid z_l \mid^2\right) - D\left(\frac{2\pi k}{L}\right)^2 z_k + \xi_{zk}\,. \tag{36}$$

The equation for the Fourier component corresponding to $\boldsymbol{k} = 0$ is much simpler and reads:

$$\frac{\partial z_0}{\partial t} = iz_0 + z_0\left(K - \mid z_0 \mid^2 - \sum_{l\neq 0} \mid z_l \mid^2\right) + \xi_{z0}\,. \tag{37}$$

Eq. (37) says that $\mid z_0 \mid$ becomes macroscopically large at the steady state if $(K - \mid z_0 \mid^2 + \sum_{l\neq 0} \mid z_l \mid^2)\rangle 0$. Unlike the equation for the evolution of the local fluctuation (Eq. (36)) there is no linear term in Eq. (37) which is able to control the stability of the process. This stability is ensured only by the nonlinear term in the dynamics. On the basis of Eqs. ((36), (37) according to the Ito rules, we obtain the evolution equations for the square of modulus of z_k. The equations for the modulus at a stationary state read:

$$\mid z_0 \mid^2\left(K - A - \mid z_0 \mid^2\right) + \frac{\varepsilon C_0}{V} = 0\,, \tag{38a}$$

$$\mid z_k \mid^2\left(K - D\left(\frac{2\pi k}{L}\right)^2 - A - \frac{\mid z_0 \mid^2}{V}\right) + \frac{\varepsilon C_k}{V} = 0\,, \tag{38b}$$

where

$$A = \sum_{k'\neq 0} \mid z_{k'} \mid^2\,. \tag{38c}$$

The formal solution of Eqs. (38 a,b) may be written as:

$$\mid z_0 \mid^2 = \frac{K - A + \sqrt{(K-A)^2 + 4\varepsilon C_0/V}}{2}\,, \tag{39a}$$

$$\mid z_k \mid^2 = \frac{\varepsilon}{V}\frac{C_k}{D(\frac{2\pi k}{L})^2 + \mid z_0 \mid^2 + A - K}\,. \tag{39b}$$

For consistency of Eqs. (39) the following relationship should be satisfied:

$$A = \frac{\varepsilon}{V}\sum_{k\neq 0}\frac{C_k}{D(\frac{2\pi k}{L})^2 + m^2}\,, \tag{40}$$

where

$$m^2 = \mid z_0 \mid^2 + A - K = \frac{A - K + \sqrt{(K-A)^2 + 4\varepsilon C_0}}{2}\,. \tag{41}$$

For the assumed form of noise (Eqs. (3), (4)) the integration in Eq. (40) may be analytically done [10] leading to:

$$A = \frac{\varepsilon}{4m\sqrt{D}} \exp\left(\frac{(m\Lambda)^2}{4D}\right)\left(1 - \Phi\left(\frac{m\Lambda}{2\sqrt{D}}\right)\right) \quad \text{for } d = 1\,, \tag{42a}$$

$$A = -\frac{\varepsilon}{4mD} \exp\left(\frac{(m\Lambda)^2}{4D}\right) Ei\left(-\frac{(m\Lambda)^2}{4D}\right) \quad \text{for } d = 2\,, \tag{42b}$$

and

$$A = \frac{\varepsilon m}{2\pi^2 D}\left(\frac{\sqrt{\pi}}{m\Lambda} - \frac{\pi}{2\sqrt{D}} \exp\left(\frac{(m\Lambda)^2}{4D}\right)\left(1 - \Phi\left(\frac{m\Lambda}{2\sqrt{D}}\right)\right)\right) \quad \text{for } d = 3\,, \tag{42c}$$

where Φ and Ei denote the probability integral and the logarithmic integral defined as follows:

$$\Phi(x) = \frac{2}{\pi} \int_0^x \exp(-t^2)dt\,,$$

$$Ei(x) = -\int_{-x}^{\infty} \frac{\exp(-t)}{t} dt\,.$$

It is worthwhile to discuss the cases $d = 1$ and $d = 3$ separately because the systems behavior in these cases is different. For simplicity let us assume that Λ is small. Now the expressions for A may be approximated as follows:

$$A = \frac{\varepsilon}{4m\sqrt{D}} \qquad for\ \ d = 1\,, \tag{43}$$

and

$$A = \frac{\varepsilon}{2\pi^2 D} \frac{\sqrt{\pi}}{\Lambda} \qquad for\ \ d = 3\,. \tag{44}$$

Let us consider the case of large K, so the system is expected to exhibit an oscillatory behavior. Eq. (38a) may be rewritten in the form:

$$m^2(m^2 + K - A) = \frac{\varepsilon C_0}{V}\,. \tag{45}$$

It can be easily solved by a symbolic algebra program, but such solution is tedious and hardly readable. Therefore let us discuss the approximate solution, the physical meaning of which is clear.

In the case of $d = 3$ one may assume that both A and m are small if compared with K and then the solution reads:

$$m \cong \sqrt{\frac{\varepsilon C_0}{VK}}\,. \tag{46}$$

Therefore $| z_0 |^2$ is approximately equal to K, which means that the system is exhibiting coherent oscillations in space.

For $d = 1$ A is a function of m so the only approximation one can make is to neglect m^2 as small if compared with K. Now the solution of Eq. ((45) is:

$$m \cong \frac{1}{2K}\left(\frac{\varepsilon}{4\sqrt{D}} + \sqrt{\left(\frac{\varepsilon}{4\sqrt{D}}\right)^2 + \frac{4K\varepsilon C_0}{V}}\right). \tag{47}$$

and

$$| z_0 |^2 \cong m^2 + K\frac{\sqrt{1 + \frac{64KC_0D}{\varepsilon V}} - 1}{\sqrt{1 + \frac{64KC_0D}{\varepsilon V}} + 1}. \tag{48}$$

Thus in $d = 1$ case the amplitude of coherent oscillations is small and related to volume and the strength of noise.

The comparison between the results obtained for $d = 1$ and $d = 3$ supports the picture we discussed in the previous chapter: it is always possible to find, even in a reduced dimensionality system, the region of the parameters in which the radius of limit cycle is different from zero. However for one dimensional case the phase fluctuations always destroy the coherent behavior after sufficiently long time. Contrary, for three dimensional systems the oscillating state lasts forever, even if the phase fluctuations, give limitation on the region in which the amplitude is stable.

4. Conclusions

Considering a specific example of a stochastic nonlinear chemical system, which exhibits oscillatory behavior, we discussed how the spatial coherence of the time evolution depends on system's dimensions.

We have shown that it is convenient to define the cutoff associated to the coarse graining procedure directly at the level of noise correlation function. The introduction of spatial correlations of noise is necessary in order to give a meaning to the stochastic Ito equation for the amplitude. This equation cannot be rigorously derived for an uncorrelated noise. A few different decoupling approximations have been used in order to solve the stochastic differential equations describing system's evolution. The approximations lead to the conclusion that coherent oscillatory state is stable in three dimensions, whereas for lower dimensionalities it is destroyed by the presence of local fluctuations. It is also interesting to notice that various approximations predict different amplitude of the limit cycle. The result of small noise expansion (Eq. (10)) says that the amplitude is enlarged by the presence of noise. The influence of noise is significantly reduced in the nonlinear regime as the result of competition between the repulsive barrier effect ($\frac{\varepsilon C(0)}{2\rho}$ term) and the nonhomogeneous phase fluctuations (Eqs. (32)–(34)). Both terms depend on noise strength and on the characteristic length of the spatial correlations of noise. The first one, by definition, the second because at the steady state there is no intrinsic length associated with the fluctuations. We have obtained that the compensation of these two effects is at the basis of the validity of a phenomenological theory (*i.e.* the theory obtained in the limit of vanishing noise amplitude). On the other hand the absence of compensation in the transient behavior gives rise to various, new phenomena, which are not predicted by phenomenology.

REFERENCES

[1] P. Gray, G. Nicolis, F. Baras, P. Borckmans, S.K. Scott, *Spatial inhomogeneities and transient behaviour in chemical kinetics*, Manchester University Press 1989; *Physica* **A188** No 1–3 (1992).

[2] L. Schimansky-Geier, A.S. Mikhailev, W. Ebeling, *Ann. Phys.* (Leipzig) **40**, 277 (1983); F. de Pasquale, J. Gorecki, J. Popielawski, *J. Phys.* **A25**, 433 (1992).

[3] Y. Kuramoto, T. Tsuzuki, *Prog. Theor. Phys.* **55**, 356 (1976); Y. Kuramoto, T. Yamada, *Prog. Theor. Phys.* **56**, 724 (1976).

[4] G.I. Sivahinsky, *Acta Astronautica* **4**, 1177 (1977); G.I. Sivahinsky, *Acta Astronautica* **6**, 569 (1979).

[5] Y. Kuramoto, *Extended Phasedynamics Approach to Pattern Evolution* in Ref. [1].

[6] D. Mermin, H. Wagner, *Phys. Rev.* **122**, 345 (1961).

[7] J. Gorecki in *Far from Equilibrium Dynamics of Chemical Systems*, Eds.: J. Gorecki *et al.*, World Scientific, Singapore 1994.

[8] Y. Kuramoto, *Chemical Oscillations, Waves and Turbulence*, Springer, Berlin 1984.

[9] C.W. Gardiner, *Handbook of Stochastic Methods*, Springer, Berlin 1983.

[10] I.S. Gradshteyn, I.M. Ryzhik,*Table of Integrals, Series and Products*, Academic Press, 1992.