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Long memory, fractal statistics, and Anderson localization for chemical waves and patterns with random propagation velocities

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An analytic approach is developed for computing the moments of concentration fields in a spatially inhomogeneous chemical system subject to environmental fluctuations, based on phase linearization. It is shown that the environmental fluctuations lead to Anderson localization. If in the absence of environmental fluctuations the system displays chemical waves periodic in space and time, then in the presence of fluctuations the waves become localized in time and space. Two limit cases exist: for homogeneous chemical systems displaying chemical oscillations, the environmental fluctuations lead to damped oscillations, i.e., to temporal localization, whereas for structured periodic patterns the localization occurs only in space. The validity of the suggested approach is tested by investigating the behavior of one-dimensional reaction-convection systems subject to time-dependent and space-independent velocity fluctuations. Computations are performed in the case of non-Markovian Gaussian perturbations of the velocity field. Both analytical and numerical calculations show that the Anderson localization of the concentration patterns is very strong for non-Markovian fluctuations with long memory characterized by correlation functions of the negative power-law type. For infinite memory the attenuation factors are Gaussian. For self-similar fractal random processes with long but finite memory, the localization is less strong and the attenuation factor is given by a compressed exponential and has a shape intermediate between a Gaussian and an exponential. Finally, for Markovian or independent random processes the localization is weak and the attenuation is exponential. We suggest an experiment for testing the predicted theoretical results and discuss the possibilities of generalizing the theory for reaction-convection systems with thermal fluctuations and for Lévy noise by using the Shlesinger-Hughes renormalization technique.
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I. INTRODUCTION

Anderson localization, i.e., the damping of a quantum wave function in a disordered system, has been studied within the context of quantum theory of condensed systems [1]. Its understanding is of fundamental importance for the explanation of the electronic properties of disordered solids [2]. A temporal analog of Anderson localization is the stochastic narrowing of line shapes in spectroscopy [3]. More recently, the localization effect has been shown to exist also for macroscopic classical systems, for instance, in the case of electromagnetic or acoustic waves propagating in a disordered medium [4]; its study has revealed some interesting features of the interaction between the nonlinear behavior and the disordered structure of macroscopic systems and has been the basis of some applications, for example, in biomedical engineering [5]. Special attention has been paid to the study of wave propagation in disordered media obeying fractal statistics [6]. As far as we know, the possible existence of Anderson localization has not been discussed in theoretical and experimental investigations of nonlinear chemical dissipative structures, chemical waves, and patterns. Articles of this subject deal mainly with purely dissipative reaction-diffusion systems for which the reversible (convective) component of motion is neglected; for such systems, Anderson localization is not significant. On the other hand, in the literature of chemical engineering, much attention has been paid to the study of the waves and patterns generated by the balancing between the convective and diffusive transport and the chemical reactions operated far from equilibrium [7]. However, the various phenomena investigated, although rather complex, do not include Anderson localization. The purpose of this paper is to present a theoretical investigation concerning Anderson localization of a structured chemical system with a fluctuating propagation speed. We are interested in the effects of long memory and fractal statistics on the localization.

II. EVOLUTION EQUATIONS

Let us consider a multicomponent open chemical system described by the deterministic kinetic equations

$$R_l = R_l(\mathbf{C}), \quad l = 1,2,\ldots, \tag{1}$$

where $C_1(t), C_2(t), \ldots$ are the concentrations at time t of the different chemicals that make up the system and $R_l(\mathbf{C})$, $l = 1,2,\ldots$, are net reaction rates. The concentration fields in the system are the solution of the balance equations

$$\partial C_l(\mathbf{r},t)/\partial t + \nabla \cdot \mathbf{J}_l = R_l(\mathbf{C}), \quad l = 1,2,\ldots, \tag{2}$$

where $\mathbf{J}_l$ are the mass fluxes of different chemicals making up the system. A complete description of the process can be given in terms of the balance equations (2), together with the hydrodynamic equations of the system that describe the mainstream flow and with the constitutive equations that express the dependence of the mass fluxes $\mathbf{J}_l$ on the state variables of the system. The time and space evolution of the concentration fields attached to the different chemicals of the system can be computed, at least in principle, by means of the integration of the coupled evolution equations for suitable initial and boundary conditions.

The solutions of the evolution equations (2) depend on a set of parameters $q_1(\mathbf{r},t), q_2(\mathbf{r},t),\ldots$, that, in the presence of environmental fluctuations, are stochastic functions of space and time. For example, these parameters may be the components of the mainstream velocity at the entrance in the system or the input or output fluxes of the different chemicals present in the system. In general, the different concentration fields $C_l(\mathbf{r},t)$, $l=1,2,\ldots$ are functionals of these parameters and depend on the whole previous time evolution of $q_1(\mathbf{r},t), q_2(\mathbf{r},t),\ldots$:

$$C_l(\mathbf{r},t)=\mathcal{C}_l[(\mathbf{r},t);q_1(\mathbf{r}',t'),q_2(\mathbf{r}',t'),\ldots],\quad l=1,2,\ldots\ . \tag{3}$$

The functional relations (3) can be determined by solving the balance equations (2) with suitable initial and boundary conditions.

A particular problem that has been extensively studied in the literature is that of chemical waves or patterns that emerge in the case when the parameters $q_1(\mathbf{r},t), q_2(\mathbf{r},t),\ldots$ are kept constant. In this case the functional relations (3) reduce to

$$C_u(\mathbf{r},t)=\mathcal{C}_u[\omega(\mathbf{k},q_1^0,q_2^0,\ldots)t-\mathbf{k}(q_1^0,q_2^0,\ldots)\cdot\mathbf{r}], \tag{4}$$

where the parameters $q_1(\mathbf{r},t), q_2(\mathbf{r},t),\ldots$ are assumed to be constant:

$$q_1(\mathbf{r},t)=q_1^0,\quad q_2(\mathbf{r},t)=q_2^0,\ldots, \tag{5}$$

and $\mathcal{C}_u=\mathcal{C}_u(\Theta_u)$ is a periodic function of the phase factor

$$\Theta_u=\omega(\mathbf{k},q_1^0,q_2^0,\ldots)t-\mathbf{k}(q_1^0,q_2^0,\ldots)\cdot\mathbf{r}. \tag{6}$$

The systems described by Eqs. (4)–(6) display concentration waves that are periodic functions in both space and time. A special situation is that of stationary periodic patterns, for which the concentration fields are periodic in space and time independent; this case corresponds to zero frequency.

In this article we are interested in the study of the more complicated situation where the parameters $q_1(\mathbf{r},t), q_2(\mathbf{r},t),\ldots$ fluctuate in a random way around the stationary values $q_1^0, q_2^0,\ldots$. We express $q_1(\mathbf{r},t), q_2(\mathbf{r},t),\ldots$ in the form

$$q_j(\mathbf{r},t)=q_j^0+\Delta q_j(\mathbf{r},t),\quad j=1,2,\ldots, \tag{7}$$

where $\Delta q_j(\mathbf{r},t)$, $j=1,2,\ldots$, are the random components of the parameters $q_1(\mathbf{r},t), q_2(\mathbf{r},t),\ldots$, and assume that the stochastic properties of the random functions are known and characterized in terms of a probability density functional

$$\mathfrak{P}[\Delta\mathbf{q}(\mathbf{r}',t')]\mathfrak{D}[\Delta\mathbf{q}(\mathbf{r}',t')]$$

$$\text{with}\ \overline{\underline{\int\int}}\,\mathfrak{P}[\Delta\mathbf{q}(\mathbf{r}',t')]\mathfrak{D}[\Delta\mathbf{q}(\mathbf{r}',t')]=1, \tag{8}$$

where $\mathfrak{D}[\Delta\mathbf{q}(\mathbf{r}',t')]$ is a suitable integration measure over the space of functions $\Delta q_1(\mathbf{r}',t'),\Delta q_2(\mathbf{r}',t'),\ldots$ and $\overline{\underline{\int\int}}$ stands for the operation of path integration. In this case a periodic solution of the form (4) does not exist anymore. The concentration fields are nonlinear functionals of the fluctuating components of the parameters $q_1(\mathbf{r},t), q_2(\mathbf{r},t),\ldots$:

$$C_u(\mathbf{r},t)=\mathfrak{C}_u[(\mathbf{r},t),\Delta\mathbf{q}(\mathbf{r}',t')],\quad l=1,2,\ldots\ . \tag{9}$$

Our purpose is to evaluate the moments $\langle C_{u_1}(\mathbf{r},t_1)C_{u_2}(\mathbf{r}_2,t_2)\cdots\rangle$ of the concentration fields in the presence of environmental fluctuations, that is, when the parameters $q_1(\mathbf{r},t), q_2(\mathbf{r},t),\ldots$ are random. These moments are given by the path integrals

$$\begin{aligned}\langle C_{u_1}(\mathbf{r}_1,t_1)C_{u_2}(\mathbf{r}_2,t_2)\cdots\rangle &= \overline{\underline{\int\int}}\,\mathfrak{C}_{u_1}[(\mathbf{r}_1,t_1),\Delta\mathbf{q}(\mathbf{r}',t')]\\ &\quad\times\mathfrak{C}_{u_2}[(\mathbf{r}_2,t_2),\Delta\mathbf{q}(\mathbf{r}',t')]\cdots\mathfrak{P}[\Delta\mathbf{q}(\mathbf{r}',t')]\\ &\quad\times\mathfrak{D}[\Delta\mathbf{q}(\mathbf{r}',t')].\end{aligned} \tag{10}$$

In a chemical system subject to random environmental fluctuations the observables that are usually accessible to the experimental measurements are the average concentration fields $\langle C_u(\mathbf{r},t)\rangle$, that is, the moments (10) of first order.

III. LINEAR PHASE APPROXIMATION FOR SMALL FLUCTUATIONS

For simplicity we limit ourselves to the particular case when the fluctuations of the parameters are small. At first sight a reasonable idea would be to expand the dependence (3) in a functional Taylor series around the periodic solutions corresponding to $\Delta\mathbf{q}=\mathbf{0}$ and to average the corresponding Taylor series term by term:

$$\begin{aligned}C_u(\mathbf{r},t)&=\mathcal{C}_u[\Theta_u]+\sum_j\int\int\frac{\delta}{\delta\Delta q_j(\mathbf{r}'',t'')}\\ &\quad\times\mathfrak{C}_u[(\mathbf{r},t),\Delta\mathbf{q}(\mathbf{r}',t')]\bigg|_{\Delta\mathbf{q}(\mathbf{r}',t')=\mathbf{0}}\\ &\quad\times\Delta q_j(\mathbf{r}'',t'')d\mathbf{r}''dt''+\cdots\ .\end{aligned} \tag{11}$$

Unfortunately, such an approach is not useful because it generates secular terms that lead to physically absurd results. To overcome this difficulty in this article we suggest a method of partial linearization, based on the expansion of the phase factors in terms of the fluctuating components of the parameters rather than on the expansion of the concentration fields. This method is somewhat similar to the Bogoliubov-Mitropolski [8] method of harmonic linearization used in the theory of nonlinear oscillation, to the Van Kampen cumulant expansion method of constructing the solution of stochastic differential equations [9], and to Bourret's [10], Novikov's [11], and Furutsu's [4] methods developed for the study of electromagnetic or acoustic wave propagation in random media.

We start out by considering the periodic solutions corresponding to $\Delta\mathbf{q}=\mathbf{0}$ and expand them in a Fourier series

$$C_u(\mathbf{r},t)=\mathcal{C}_u[\Theta_u]=\sum_{-\infty}^{+\infty}\mathcal{G}_u^{0(m)}\exp(im\Theta_u). \tag{12}$$

For a given realization of the environmental fluctuations, $\Delta\mathbf{q}\neq\mathbf{0}$ and the realization of the concentration fields $C_u(\mathbf{r},t)$ is no longer a periodic function. Nevertheless, it can be represented formally as the superpositions of the contributions of different amplitude and phase factors:

$$C_u(\mathbf{r},t)=\sum_{-\infty}^{+\infty}\tilde{\mathcal{G}}_u^{(m)}[\Delta\mathbf{q}(\mathbf{r}',t')]\exp\{i\tilde{\Theta}_u^{(m)}[\Delta\mathbf{q}(\mathbf{r}',t')]\}. \tag{13}$$

We emphasize that for $\Delta\mathbf{q}\neq\mathbf{0}$ the expansion (13) is no longer a Fourier series but reduces to the Fourier series (12) in the limit $\Delta\mathbf{q}\rightarrow\mathbf{0}$, that is, we have

$$\tilde{\mathcal{G}}_u^{(m)}\rightarrow\mathcal{G}_u^{0(m)},\quad \tilde{\Theta}_u^{(m)}\rightarrow m\Theta_u\quad\text{as}\quad\Delta\mathbf{q}\rightarrow\mathbf{0}. \tag{14}$$

Equation (13) is a convenient representation of the concentration field by an infinite series, which in the limit case of a nonrandom environment reduces to the Fourier series (12). In general, the representation (13) is not unique. In order to avoid any ambiguities we introduce a set of modified amplitude and phase functions, denoted by $\mathcal{G}_u^{(m)}$ and $\Theta_u^{(m)}$ and defined in such a way that the modified amplitude factors $\mathcal{G}_u^{(m)}$ are independent of the fluctuation vector $\Delta\mathbf{q}$:

$$\mathcal{G}_u^{(m)}=\mathcal{G}_u^{0(m)}\quad\text{independent of}\quad\Delta\mathbf{q}, \tag{15}$$

$$\Theta_u^{(m)}[\Delta\mathbf{q}(\mathbf{r}',t')]=\tilde{\Theta}_u^{(m)}[\Delta\mathbf{q}(\mathbf{r}',t')]-i\,\ln\{\tilde{\mathcal{G}}_u^{(m)}[\Delta\mathbf{q}(\mathbf{r}',t')]/\mathcal{G}_u^{0(m)}\}. \tag{16}$$

By using the notation in Eqs. (15) and (16) the expansion (13) becomes

$$C_u(\mathbf{r},t)=\sum_{-\infty}^{+\infty}\mathcal{G}_u^{0(m)}\exp\{i\Theta_u^{(m)}[\Delta\mathbf{q}(\mathbf{r}',t')]\}. \tag{17}$$

The main idea of our approach is that, in the case of small environmental fluctuations, the phase factors $\Theta_u^{(m)}[\Delta\mathbf{q}(\mathbf{r}',t')]$, rather than the instantaneous concentration fields $C_u(\mathbf{r},t)$, should be linearized

$$\begin{aligned}\Theta_u^{(m)}[\Delta\mathbf{q}(\mathbf{r}',t')]=m\Theta_u+\sum_j\int\int\frac{\delta}{\delta\Delta q_j(\mathbf{r}'',t'')}\\ \times\Theta_u^{(m)}[\Delta\mathbf{q}(\mathbf{r}',t')]|_{\Delta\mathbf{q}(\mathbf{r}',t')=0}\\ \times\Delta q_j(\mathbf{r}'',t'')d\mathbf{r}''dt''+\cdots.\end{aligned} \tag{18}$$

This approximation is similar to the eikonal approximation from geometrical optics and to the WKB (quasiclassical) approximation from quantum mechanics or to the abovementioned techniques from the wave theory. Unlike the "naive" expansion (11), the approximation (18) does not generate secular divergent terms. By combining Eqs. (17) and (18) we get the following expression for the instantaneous concentration fields:

$$\begin{aligned}C_u(\mathbf{r},t)=\sum_{-\infty}^{+\infty}\mathcal{G}_u^{0(m)}\exp\{im\Theta_u\}\\ \times\exp\left\{i\sum_j\int\int\varepsilon_{uj}^{(m)}(\mathbf{r}',t';\mathbf{r}'',t'')\right.\\ \left.\times\Delta q_j(\mathbf{r}'',t'')d\mathbf{r}''dt''\right\},\end{aligned} \tag{19}$$

where the integration kernels $\varepsilon_{uj}^{(m)}(\mathbf{r}',t';\mathbf{r}'',t'')$ are the functional derivatives of the phase factors $\Theta_u^{(m)}[\Delta\mathbf{q}(\mathbf{r}',t')]$:

$$\varepsilon_{uj}^{(m)}(\mathbf{r}',t';\mathbf{r}'',t'')=\left.\frac{\delta\Theta_u^{(m)}[\Delta\mathbf{q}(\mathbf{r}',t')]}{\delta\Delta q_j(\mathbf{r}'',t'')}\right|_{\Delta\mathbf{q}(\mathbf{r}',t')=\mathbf{0}}. \tag{20}$$

If the concentration fields are approximated by Eq. (19), then the path integral in Eq. (10) can be easily evaluated. We introduce the characteristic functional of the probability density functional $\mathfrak{P}[\Delta\mathbf{q}(\mathbf{r}',t')]\mathfrak{D}[\Delta\mathbf{q}(\mathbf{r}',t')]$:

$$\begin{aligned}\mathfrak{G}[\mathbf{K}(\mathbf{r}',t')]=\left\langle\exp\left\{i\int\int\mathbf{K}(\mathbf{r}',t')\cdot\Delta\mathbf{q}(\mathbf{r}',t')d\mathbf{r}'dt'\right\}\right\rangle\\ =\overline{\underline{\int\int}}\exp\left\{i\int\int\mathbf{K}(\mathbf{r}',t')\cdot\Delta\mathbf{q}(\mathbf{r}',t')d\mathbf{r}'dt'\right\}\\ \times\mathfrak{P}[\Delta\mathbf{q}(\mathbf{r}'t')]\mathfrak{D}[\Delta\mathbf{q}(\mathbf{r}',t')],\end{aligned} \tag{21}$$

where $\mathbf{K}(\mathbf{r}',t')$ is a suitable vectorial test function conjugate to the vector of fluctuating environmental variables $\Delta\mathbf{q}(\mathbf{r}',t')$. It is well known from quantum field theory as well as from mathematical statistics [12] that the logarithm of the characteristic functional $\mathfrak{G}[\mathbf{K}(\mathbf{r}',t')]$ can be expressed as a multivariate functional Taylor series in terms of the different powers of the components of the test function $\mathbf{K}(\mathbf{r}',t')$ where the coefficients of the expansion are given by the cumulants $\langle\langle\Delta q_{n_1}(\mathbf{r}',t_1')\cdots\Delta q_{n_m}(\mathbf{r}_m',t_m')\rangle\rangle$ of the fluctuating environmental variables [12]:

$$\begin{aligned}\ln\mathfrak{G}[\mathbf{K}(\mathbf{r}',t')]\\ =\sum_{m=1}^{\infty}\frac{i^m}{m!}\sum_{n_1=1}^{\mathcal{A}}\cdots\sum_{n_m=1}^{\mathcal{A}}\int\int\cdots\int\int K_{n_1}(\mathbf{r}_1',t_1')\cdots\\ \times K_{n_m}(\mathbf{r}_m',t_m')\langle\langle\Delta q_{n_1}(\mathbf{r}_1',t_1')\cdots\Delta q_{n_m}(\mathbf{r}_m',t_m')\rangle\rangle\\ \times d\mathbf{r}_1'dt_1'\cdots d\mathbf{r}_m'dt_m'.\end{aligned} \tag{22}$$

By combining Eqs. (10), (19), and (21)–(22) after lengthy calculations we arrive at the following expression for the moments of the concentration fields:

$$\left\langle \prod_{\beta=1}^{\mathcal{B}} C_{u_\beta}(\mathbf{r}_\beta, t_\beta) \right\rangle = \sum_{u_1=-\infty}^{+\infty} \cdots \sum_{u_{\mathcal{B}}=-\infty}^{+\infty} \exp[\mathcal{H}_{u_1 \cdots u_{\mathcal{B}}}] \prod_{\beta=1}^{\mathcal{B}} \{\mathcal{G}_{u_\beta}^{0(m_\beta)} \exp[i m_\beta \Theta_{u_\beta}]\}, \tag{23}$$

where $\mathcal{H}_{u_1 \cdots u_B}$ is a complex phase factor depending on all cumulants of the environmental fluctuating variables

$$\mathcal{H}_{u_1 \cdots u_{\mathcal{B}}} = \ln\left\{ \left\langle \exp\left(i \sum_{\beta=1}^{\mathcal{B}} \sum_{j} \int \int \varepsilon_{u_\beta j}^{(m_\beta)}(\mathbf{r}', t'; \mathbf{r}'', t'') \Delta q_j(\mathbf{r}'', t'') d\mathbf{r}'' dt'' \right) \right\rangle \right\} = \sum_{j=1}^{\infty} i^j \mathcal{H}_{u_1 \cdots u_{\mathcal{B}}}^{(j)}, \tag{24}$$

$$\mathcal{H}_{u_1 \cdots u_{\mathcal{B}}}^{(j)} = \sum_{n_1=1}^{\mathcal{A}} \cdots \sum_{n_j=1}^{\mathcal{A}} \frac{1}{j!} \int \int \int \int d\mathbf{r}_1' dt_1' d\mathbf{r}_1'' dt_1'' \cdots \int \int \int \int d\mathbf{r}_j' dt_j' d\mathbf{r}_j'' dt_j''$$

$$\times \sum_{\beta_1=1}^{\mathcal{B}} \varepsilon_{u_{\beta_1} n_1}^{(m_{\beta_1})}(\mathbf{r}_1', t_1'; \mathbf{r}_1'', t_1'') \cdots \sum_{\beta_2=1}^{\mathcal{B}} \varepsilon_{u_{\beta_2} n_j}^{(m_{\beta_2})}(\mathbf{r}_j', t_j'; \mathbf{r}_j'', t_j'') \langle\langle \Delta q_{n_1}(\mathbf{r}_1', t_1') \cdots \Delta q_{n_j}(\mathbf{r}_j', t_j') \rangle\rangle. \tag{25}$$

Equations (23)–(25) give a systematic cumulant expansion for the contributions of the fluctuations of different orders of the environmental variables to the moments of the concentration field. This expression can be used to show that the environmental fluctuations can produce Anderson localization. Equation (24) is a Taylor expansion in terms of the different powers of the imaginary unit and in general the phase factor $\mathcal{H}_{u_1 \ldots u_{\mathcal{B}}}$ has both an imaginary and a real part

$$\mathcal{H}_{u_1 \cdots u_{\mathcal{B}}} = \mathrm{Re}(\mathcal{H}_{u_1 \cdots u_{\mathcal{B}}}) + i\ \mathrm{Im}(\mathcal{H}_{u_1 \cdots u_{\mathcal{B}}}),$$

which are made up of the contributions of the even and odd powers in the series (24), respectively. The imaginary part $\mathrm{Im}(\mathcal{H}_{u_1 \cdots u_{\mathcal{B}}})$ produces an additional contribution to the phase factors $m\Theta_u$ attached to the different harmonics of the Fourier series (12), which results in a change of the frequency and of the wave vector of the oscillations. On the other hand, the real part $\mathrm{Re}(\mathcal{H}_{u_1 \cdots u_{\mathcal{B}}})$ may lead to either an increase or a decrease of the concentration fields, depending on whether $\mathrm{Re}(\mathcal{H}_{u_1 \cdots u_{\mathcal{B}}}) > 0$ or $\mathrm{Re}(\mathcal{H}_{u_1 \cdots u_{\mathcal{B}}}) > 0$, respectively. The general assumptions made in this section are not detailed enough to evaluate the sign of the real part of the complex phase factor. However, in the particular case investigated in the following sections we have $\mathrm{Re}(\mathcal{H}_{u_1 \cdots u_{\mathfrak{B}}}) < 0$, that is, the concentration fields display damping, which corresponds to Anderson localization. In general, for $\mathrm{Re}(\mathcal{H}_{u_1 \cdots u_{\mathcal{B}}}) < 0$, the localization occurs in both space and time. In the special case where the system without environmental fluctuations is homogeneous and displays periodic oscillations in time, in Eq. (6) for the phase Θ_u we have $\mathbf{k} = \mathbf{0}$ and the only effect of environmental fluctuations is the temporal damping of the oscillations. For example, such an effect may be observed in a perfectly stirred continuous reaction (CSTR) with a random flow rate. Another particular case corresponds to the situation where the system without fluctuations displays a stationary concentration profile periodic in space. In this case the system displays localization in space in the presence of environmental fluctuations. This effect may be observed in the case of an oscillatory chemical reaction operated in an ideal tubular reactor, the case investigated in detail in the remaining sections of the article.

IV. CONCENTRATION FIELDS IN IDEAL TUBULAR REACTORS

The general approach suggested in the preceding section to analyze the influence of environmental fluctuations on a chemical wave or pattern has been inspired by similar approaches suggested in the literature for electromagnetic and acoustic waves. In both cases the linear phase approximation is used to avoid the occurrence of the spurious secular terms and the main assumptions are the same for the two types of models. Despite this formal analogy, the detailed structure of the mathematical equations is different for the two types of models, mainly due to the different origin of the periodic behavior. For an acoustic or electromagnetic wave the periodic behavior is generated by an inertial effect due to the mathematical structure of Newton's or Maxwell's equations; for these waves the oscillations exist even when the evolution equations are linear. For a chemical system, however, the origin of the oscillations is different: It is a nonequilibrium effect generated by the nonlinear feedback coupling among the different individual reaction steps. Due to the intrinsic nonlinearity of the kinetic equations, the evolution of chemical waves or patterns in a random environment is much harder to study.

For a rather particular case of structured chemical systems a detailed analysis is, however, possible. This case corresponds to a reaction-convection system characterized by a mainstream flow characterized with a possibly time-dependent but space-independent overall velocity, which is the same for all chemicals in the system and for which the contribution of molecular or turbulent diffusion can be neglected. Although at first sight these constraints seem to be very restrictive, they are commonly discussed in the literature for the description of a common device used for the experimental study of chemical processes, the reaction tube [13]. A reaction tube (or tubular reactor) is basically a pipe along which a reaction mixture flows under controlled conditions. The dimensions of the device, as well as the other parameters of the system such as the flow rate and the temperature or the pressure, are chosen in such a way that the main contribution to the mass transport is given by the mainstream flow, the molecular and turbulent diffusion can be neglected, and the flow velocity is basically the same at any position along the pipe. If the velocity along the reaction tube at time t is $v(t)$ then the evolution equations (2) reduce to

$$\frac{\partial}{\partial t} C_l(\mathbf{r},t)+v(t)\,\frac{\partial}{\partial x}\,C_l(\mathbf{r},t)=R_l(\mathbf{C}),\quad l=1,2,\ldots\,. \tag{26}$$

A typical experiment in a reaction tube is carried out by continuously introducing known amounts of different chemicals at the entrance of the reaction tube $x=x_0$. If the input concentrations of the different chemicals at time t, $C_l(x=x_0,t)=C_l^{\mathrm{in}}(t)$, $l=1,2,\ldots$, are known functions of time, then they provide a set of boundary conditions for the partial differential equations (26)

$$\mathbf{C}(x=x_0,t)=\mathbf{C}^{\mathrm{in}}(t)\quad\text{with}\quad \mathbf{C}^{\mathrm{in}}(t)=[C_l^{\mathrm{in}}(t)]. \tag{27}$$

The characteristics of the partial differential equations (5) are the solutions of the ordinary differential equations

$$dt=\frac{dC_l}{R_l(\mathbf{C})}=\frac{dx}{v(t)},\quad l=1,2,\ldots\,. \tag{28}$$

The set of characteristic equations (28) is made up of a set of deterministic evolution equations characterizing the time evolution of a homogeneous chemical system with the rate equations given by Eq. (1),

$$\frac{dC_l}{dt}=R_l(\mathbf{C})\quad\text{with}\quad \mathbf{C}(t=0)=\mathbf{C}_0,\quad l=1,2,\ldots, \tag{29}$$

as well as by the additional relationship

$$dx/dt=v(t), \tag{30}$$

which gives a Lagrangian description of the flow process. In Eqs. (29) $R_l(\mathbf{C})$ are nonlinear functions of the composition vector and because of that Eqs. (29) can be solved analytically only in exceptional cases. In the following, however, we assume that the solutions of these equations

$$\mathbf{C}(t)=\boldsymbol{\Xi}(\mathbf{C}_0;t),\quad\text{i.e.,}\quad C_l(t)=\Xi_l(\mathbf{C}_0;t),\quad l=1,2,\ldots, \tag{31}$$

are known for any values of the initial concentrations and of the time variable; for instance, they have been determined by numerical integration or from the experimental analysis of the system.

From the theory of partial differential equations it follows that the general solutions of the balance equations (26) can be expressed as arbitrary functions of the solutions (31) of the homogeneous kinetic equations (29). These arbitrary functions can be determined in terms of the boundary conditions (27). A simple calculation leads to the following expression for the time and space variation of the concentration fields along the reaction tube (similar computations are presented in the literature of chemical engineering [13,14]):

$$\mathbf{C}(x,t)=\boldsymbol{\Xi}[\mathbf{C}^{\mathrm{in}}(\eta(x,t));t-\eta(x,t)], \tag{32}$$

where $\eta(x,t)$ is the solution of the functional equation

$$x=\int_{\eta(x,t)}^{t} v(t')dt' \tag{33}$$

and $\boldsymbol{\Xi}(\mathbf{C}_0;t)$ is the vector of the solutions of the evolution equations (29) for the homogeneous system corresponding to the initial condition $\mathbf{C}(t=0)=\mathbf{C}_0$. The vector of solutions (32) of the evolution equations (26) is determined completely by the solution $\boldsymbol{\Xi}(\mathbf{C}_0;t)$ of the kinetic equations (29) of the homogeneous system and by the function $\eta(x,t)$, which depends on the velocity $v(t)$ along the reaction tube. If the solution of the ordinary differential equations is known, then Eq. (32) allows us to make predictions concerning space and time dynamics of the concentration fields along the reaction tube.

V. ASYMPTOTIC BEHAVIOR WITHOUT ENVIRONMENTAL FLUCTUATIONS

Analytical solutions similar to the solution (32) of the balance equation (26) have been reported; Eq. (32) includes as a particular case the expressions for the stationary concentration profiles along a reaction tube presented in the chemical engineering literature [13,14]. This particular case corresponds to the situation where the kinetic equations (29) for a homogeneous system have a unique stationary point $\mathbf{C}=\boldsymbol{\Xi}^*(\mathbf{C}_0)$ that is globally stable. In this case for large time the transient solutions of the kinetic equations tend towards $\mathbf{C}=\boldsymbol{\Xi}^*(\mathbf{C}_0)$:

$$\lim_{t\to\infty}\boldsymbol{\Xi}(\mathbf{C}_0;t)=\boldsymbol{\Xi}^*(\mathbf{C}_0) \tag{34}$$

independently of t. If the same experiment is carried out in a reaction tube, the propagation speed is time independent

$$v=v_0, \tag{35}$$

and the input concentrations are independent of time

$$\mathbf{C}^{\mathrm{in}}(t)=\mathbf{C}_0, \tag{36}$$

then in the long run the concentration profiles along the reaction tube become stationary. In this case we have

$$\eta(x,t)=t-x/v_0 \tag{37}$$

and from Eqs. (32)–(37) it follows that

$$\lim_{t\to\infty}\mathbf{C}(x,t)=\mathbf{C}^*(x) \tag{38}$$

independently of t, where the vector $\mathbf{C}^*(x)$ of stationary concentration profiles is given by the transient solution of the kinetic equations of the homogeneous system with the time variable replaced by the residence time of the fluid elements in the reaction tube at position x,

$$\mathbf{C}^*(x)=\boldsymbol{\Xi}(\mathbf{C}_0;\zeta(x)), \tag{39}$$

with

$$\zeta(x)=x/v_0. \tag{40}$$

In particular, for very long reaction tubes $x\to\infty$, the vector of stationary concentration profiles tends towards the stationary point of the kinetic equations (1) of the homogeneous system

$$\lim_{x\to\infty}\mathbf{C}^*(x)=\boldsymbol{\Xi}^*(\mathbf{C}_0) \tag{41}$$

independently of x.

In the following we apply our general relation to the more interesting situation in which, in the long run, the homogeneous system tends towards a normal kinetic regime that is variable in time, independent of the initial preparation of the system, and corresponds to a stable limit cycle

$$\lim_{t\to\infty}\mathbf{C}(t)=\boldsymbol{\Xi}^*(t) \tag{42}$$

independently of $\mathbf{C}_0$. We start out by considering the particular case where the velocity along the reaction tube is constant and therefore the function $\eta(x,t)$ is given by Eq. (37). In this case, after a sufficiently large time the concentrations along the reaction tube become stationary (i.e., time independent) and are functions only of the position x. In particular, if for the homogeneous system the asymptotic behavior corresponds to a stable limit cycle, then the vectorial function $\boldsymbol{\Xi}^*(t)$ is made up of components that are periodic functions of time [15]. In this case the corresponding inhomogeneous system displays periodic stationary chemical patterns along the reaction tube, characterized by a periodic space variation of the corresponding chemicals

$$\lim_{t\to\infty}\mathbf{C}(x;t)=\mathbf{C}^*(x) \tag{43}$$

independently of t, where the stationary vector of the concentration fields $\mathbf{C}^*(x)$ is given by

$$\mathbf{C}^*(x)=\boldsymbol{\Xi}^*(\zeta(x)). \tag{44}$$

We express the components of the normal solution $\boldsymbol{\Xi}^*(t)$ in a temporal Fourier series

$$\Xi_u^*(t)=\sum_{-\infty}^{+\infty} g_u^{(m)}\exp(im\omega t)=\widetilde{C}_u^*+\sum_{m=1}^{\infty}A_u^{(m)}\cos(m\omega t-\varphi_u^{(m)}), \tag{45}$$

where $\omega/2\pi$ is the frequency of the limit cycle, the terms

$$\widetilde{C}_u^*=\frac{\omega}{2\pi}\int_{-\pi/\omega}^{+\pi/\omega}C_u^*(t+a)da \tag{46}$$

are the temporal averages of the concentrations, and

$$g_u^{(m)}=\frac{\omega}{2\pi}\int_{-\pi/\omega}^{+\pi/\omega}\exp(-i\omega ma)C_u^*(t+a)da, \tag{47}$$

$$A_u^{(m)}=\frac{\omega}{\pi}\left\{\left[\int_{-\pi/\omega}^{+\pi/\omega}\sin(\omega ma)C_u^*(t+a)da\right]^2+\left[\int_{-\pi/\omega}^{+\pi/\omega}\cos(\omega ma)C_u^*(t+a)da\right]^2\right\}^{1/2}, \tag{48}$$

$$\varphi_u^{(m)}=\arctan\left\{\int_{-\pi/\omega}^{+\pi/\omega}\sin(\omega ma)\times C_u^*(t+a)da\bigg/\int_{-\pi/\omega}^{+\pi/\omega}\cos(\omega ma)\times C_u^*(t+a)da\right\} \tag{49}$$

are the complex and real amplitudes and the phase angles of the different harmonics, respectively. The stationary concentration profiles along the reaction tube can be expressed by a similar spatial Fourier series

$$C_u^*(x)=\sum_{-\infty}^{+\infty} g_u^{(m)}\exp(imkx)=\widetilde{C}_u^*+\sum_{m=1}^{\infty}A_u^{(m)}\cos(mkx-\varphi_u^{(m)}), \tag{50}$$

where the wave number k is given by the dispersion relation

$$k=v_0/\omega. \tag{51}$$

Thus we have shown that in the long run the concentration profile is a time-independent periodic function of position.

Strictly speaking, for a stable limit cycle the normal solutions $\boldsymbol{\Xi}^*(t)$ of the kinetic equations (1) of the homogeneous system are different for different initial conditions. However, their shape is identical, that is, they are the same up to a constant phase difference. In mathematical terms, given two normal solutions $\boldsymbol{\Xi}_{(1)}^*(t)$ and $\boldsymbol{\Xi}_{(2)}^*(t)$, the solution $\boldsymbol{\Xi}_{(1)}^*(t)$ can be obtained from $\boldsymbol{\Xi}_{(2)}^*(t)$ and vice versa by changing the origin of the time axis. The two solutions are characterized by the same amplitude factors $\widetilde{C}_u^*$ and $A_u^{(m)}$ and the differences between their phases $\varphi_{u(1)}^{(m)}$ and $\varphi_{u(2)}^{(m)}$ is independent of time and proportional to the harmonic label m. Similarly, the stationary concentration profiles given by Eq. (27) have the same shape for any values of the boundary conditions at $x=x_0$ and only their phases are different.

VI. ANDERSON LOCALIZATION IN TUBULAR REACTORS

The next step in our analysis is to consider the more general case for which the speed along the reaction tube is made up of two components: a constant component v_0 and a randomly fluctuating component $\Delta v(t)$,

$$v(t)=v_0+\Delta v(t). \tag{52}$$

As we are interested in the influence of long memory on localization, we assume that the stochastic process describing the random behavior of the fluctuating component $\Delta v(t)$ may have certain self-similar statistical fractal features. We make the following choices: (a) the moments and cumulants of $\Delta v(t)$ are finite and the statistical fractal features are given by the shape of the correlation functions, which are assumed to be described by negative power laws of time, and (b) the moments and cumulants of $\Delta v(t)$ are infinite and the stochastic process is of the Lévy type. In this article we limit ourselves to the study of case (a); work on Lévy statistics is in progress and will be presented elsewhere. We assume that the fluctuations of velocity are symmetric, small, and described by a stationary Gaussian stochastic process. The stochastic properties of a Gaussian stochastic process are completely characterized by its cumulants of first and second order. For Gaussian statistics, since the stochastic process is symmetric and stationary, the cumulant of first order of $\Delta v(t)$, $\langle\langle \Delta v(t)\rangle\rangle$, which is the same as the average value $\langle \Delta v(t)\rangle$, is equal to zero,

$$\langle\langle \Delta v(t)\rangle\rangle=\langle \Delta v(t)\rangle=0, \tag{53}$$

and the cumulant of second order of $\Delta v(t)$, $\langle\langle \Delta v(t_1)\Delta v(t_2)\rangle\rangle$, which is the same as the correlation function $\langle \Delta v(t_1)\Delta v(t_2)\rangle$, is symmetric and depends only on the absolute value of the time differences and is independent of the individual times

$$\langle\langle \Delta v(t_1)\Delta v(t_2)\rangle\rangle=\langle \Delta v(t_1)\Delta v(t_2)\rangle=\Phi(|t_1-t_2|). \tag{54}$$

Different expressions for the correlation function $\Phi(|t_1-t_2|)$ correspond to different types of stochastic processes. If $\Phi(|t_1-t_2|)$ is independent of time, then the process has infinite memory, whereas for a negative power-law dependence the process has long but finite memory. Similarly, for a Markovian process with short memory the correlation function is an exponential and for an independent random process without memory is given by a δ function.

The probability of a fluctuating path attached to the Gaussian stochastic process introduced before can be characterized by a probability density functional of the Wiener type:

$$\begin{aligned}\mathfrak{P}[\Delta v(t')]\mathfrak{D}[\Delta v(t')] &=\exp\left\{-\frac{1}{2}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}G[|t_1-t_2|]\right.\\ &\quad\left.\times\Delta v(t_1)\Delta v(t_2)dt_1dt_2\right\}\mathfrak{D}[\Delta v(t')],\end{aligned} \tag{55}$$

where $\mathfrak{D}[\Delta v(t')]$ is the usual Gaussian Wiener integration measure [12] and $G(x)$ is the solution of the convolution equation

$$\int_0^x G(y)\Phi(x-y)dy=\delta(x). \tag{56}$$

Due to the fluctuations of the velocity along the reaction tube the concentrations of the different chemicals are fluctuating quantities. For a given realization of the stochastic process the concentrations are no longer stationary but depend on both space and time. Nevertheless, in the long run their time and space variation can be expressed in terms of the Fourier representation (50) of the limit cycle corresponding to the chosen homogeneous system

$$\mathbf{C}_u^*[\Delta v(t');x,t]=\sum_{-\infty}^{+\infty} g_u^{(m)}\exp(im\omega\{t-\eta[\Delta v(t');x,t]\}). \tag{57}$$

In this case both the random realizations $\mathbf{C}_u^*[\Delta v(t');x,t]$ and the function $\eta[\Delta v(t');x,t]$ are functionals of the random contribution $\Delta v(t)$ to the velocity along the reaction tube. The macroscopic concentration fields are ensemble averages with respect to the fluctuations of $\Delta v(t)$. These ensemble averages express the mean behavior of a statistical ensemble of realizations of the type (57) and can be expressed as a path integral in terms probability density functional (55),

$$\begin{aligned}\langle \mathbf{C}_u^*[\Delta v(t');x,t]\rangle &=\overline{\int\int}\sum_{-\infty}^{+\infty} g_u^{(m)}\exp(im\omega\{t-\eta[\Delta v(t');x,t]\})\\ &\quad\times\mathfrak{P}[\Delta v(t')]\mathfrak{D}[\Delta v(t')],\end{aligned} \tag{58}$$

where $\overline{\int\int}$ stands for the operation of path integration.

Since we have assumed that the fluctuations of the component $\Delta v(t)$ are small, most realizations of $\Delta v(t)$ are smaller than the constant component v_0 and the functional $\eta[\Delta v(t');x,t]$ can be approximated by the sum of the first two terms in its functional Taylor expansion

$$\eta[\Delta v(t');x,t]\approx\eta[\Delta v(t')=0;x,t]+\int\varepsilon(x,t,t'')\Delta v(t'')dt'', \tag{59}$$

where the coefficient $\varepsilon(x,t,t'')$ is given by the functional derivative

$$\varepsilon(x,t,t'')=\frac{\delta\eta[\Delta v(t')=0;x,t]}{\delta\Delta v(t'')}. \tag{60}$$

The first term in the expansion (59) is given by the function $\eta[\Delta v(t');x,t]$ corresponding to a constant velocity v_0 and can be computed from Eq. (37):

$$\eta[\Delta v(t')=0;x,t]=t-x/v_0. \tag{61}$$

Similarly, the coefficient $\varepsilon(x,t,t'')$ can be computed by rewriting Eq. (33) in the form

$$x=v_0\{t-\eta[\Delta v(t');x,t]\}+\int_{\eta[\Delta v(t');x,t]}^{t}\Delta v(t')dt' \tag{62}$$

and by evaluating the variation of $\eta[\Delta v(t');x,t]$ with respect to $\delta\Delta v(t')$ and by making $\Delta v(t')=0$ in the resulting expression. After performing these computations we obtain

$$\varepsilon(x,t,t'')=\frac{1}{v_0}\left[\theta(t)-\theta\left(t-\frac{x}{v_0}\right)\right], \tag{63}$$

where $\theta(t)$ is the Heaviside step function. By using Eqs. (59)–(63) we can express the path average (58) in the form

$$\langle \mathbf{C}_u^*[\Delta v(t');x,t]\rangle=\sum_{-\infty}^{+\infty} g_u^{(m)}T^{(m)}(x,t)\exp(imkx), \tag{64}$$

where $T^{(m)}(x,t)$ are amplitude factors given by the Gaussian functional integrals

$$\begin{aligned}T^{(m)}(x,t)=\overline{\underline{\int\int}}\ \exp\bigg(&-\tfrac{1}{2}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}G[|t_1-t_2|]\\ &\times\Delta v(t_1)\Delta v(t_2)dt_1dt_2\\ &+imk\int_{t-x/v_0}^{t}\Delta v(t')dt'\bigg)\mathfrak{D}[\Delta v(t')].\end{aligned} \tag{65}$$

The path integral in Eq. (42) can be evaluated analytically, resulting in

$$T^{(m)}(x)=\exp\left[-\frac{m^2\omega^2}{(v_0)^2}\mathcal{J}\left(\frac{x}{v_0}\right)\right], \tag{66}$$

independently of t, where

$$\mathcal{J}(\beta)=\int_0^{\beta}(\beta-u)\Phi(u)du. \tag{67}$$

We notice that the amplitude factors $T^{(m)}(x)$ are real and symmetric with respect to the harmonic label m $[T^{(+m)}(x)=T^{(-m)}(x)]$ and independent of time. It follows that the average concentration profiles $\langle \mathbf{C}_u^*[\Delta v(t');x,t]\rangle$ can be expressed in the form

$$\begin{aligned}\langle \mathbf{C}_u^*[\Delta v(t');x,t]\rangle&=\widetilde{C}_u^*+\sum_{m=1}^{\infty}A_u^{(m)}\cos(mkx-\varphi_u^{(m)})T^{(m)}(x)\\ &=\widetilde{C}_u^*+\sum_{m=1}^{\infty}A_u^{(m)}\cos(mkx-\varphi_u^{(m)})\\ &\quad\times\exp\left[-\frac{m^2\omega^2}{(v_0)^2}\mathcal{J}\left(\frac{x}{v_0}\right)\right],\end{aligned} \tag{68}$$

independently of t.

The superior moments of the concentration fields can be computed in a similar way. In particular, the moments of order q at position x can be written as

$$\begin{aligned}&\left\langle\prod_{\beta=1}^{q}\mathbf{C}_{u_\beta}^*[\Delta v(t');x,t]\right\rangle\\ &\quad=\overline{\underline{\int\int}}\sum_{-\infty}^{+\infty}\cdots\sum_{-\infty}^{+\infty}\prod_{\beta=1}^{q}(g_{u_\beta}^{(m)})\exp\Bigg[i\left(\sum_{\beta=1}^{q}m_\beta\right)\\ &\qquad\times\omega\{t-\eta[\Delta v(t');x,t]\}\Bigg]\mathfrak{P}[\Delta v(t')]\mathfrak{D}[\Delta v(t')].\end{aligned} \tag{69}$$

In Eq. (69) for small speed fluctuations the ensemble average can be expressed also in terms of the amplitude factors $T^{(m)}(x,t)$. After some calculations we obtain

$$\begin{aligned}&\left\langle\prod_{\beta=1}^{q}\mathbf{C}_{u_\beta}^*[\Delta v(t');x,t]\right\rangle\\ &\quad=\sum_{u_1=0}^{+\infty}\cdots\sum_{u_q=0}^{+\infty}\prod_{\beta=1}^{q}\{A_{u_\beta}^{(m_\beta)}\cos[mu_\beta kx-\varphi_{u_\beta}^{(m_\beta)}]\}T\\ &\qquad\times\exp\left(\sum_{\beta}m_\beta\right)(x),\end{aligned} \tag{70}$$

where

$$A_u^{(0)}=\widetilde{C}_u^*,\quad \varphi_u^{(0)}=0. \tag{71}$$

From the above calculations it follows that, even though for a fluctuating speed the different realizations of the concentration fields are functions of space and time, their ensemble averages are time independent. Concerning the space dependence, we notice that in the spatial Fourier series (45) each harmonic term is damped with a factor $T^{(m)}(x)$. This behavior corresponds to the Anderson localization of the reaction-convection chemical patterns. The intensity of damping of the harmonic m can be characterized by the damping factor $T^{(m)}(x)$, which, for fluctuations of the velocity field different from zero, decreases from the maximum value $T^{(m)}(x=0)=1$ to zero in the limit $t\to\infty$. In terms of this factor we can define a damping length scale $\lambda_d^{(m)}$. In analogy to the Anderson length scale from the literature [1,2], $\lambda_d^{(m)}$ corresponds to a decrease of the damping factor $T^{(m)}(x)$ from the initial value 1 to $T^{(m)}=1/e$. $\lambda_d^{(m)}$ is the solution of the equation

$$-\ln[T^{(m)}(x)]=\frac{m^2\omega^2}{(v_0)^2}\mathcal{J}\left(\frac{\lambda_d^{(m)}}{v_0}\right)=1. \tag{72}$$

The reciprocal value of $\lambda_d^{(m)}$,

$$\varepsilon_u^{(m)}=1/\lambda_d^{(m)}, \tag{73}$$

is a measure of the strength of the localization of the convection-reaction chemical patterns.

The strength of localization is determined by the type of stochastic process describing the fluctuations of the mainstream velocity. We consider the following particular cases.

(i) Systems with static disorder. For such systems the fluctuations of velocity, once they have arisen, last forever. The

stochastic process describing the speed fluctuations has infinite memory and the correlation function is constant,

$$\langle\langle \Delta v(t_1)\Delta v(t_2)\rangle\rangle = \langle \Delta v(t_1)\Delta v(t_2)\rangle = \Phi, \tag{74}$$

the damping factors have a Gaussian shape

$$T^{(m)}(x) = \exp\left[-\frac{m^2\omega^2\Phi}{(v_0)^4}\,x^2\right], \tag{75}$$

and the damping length is given by

$$\lambda_d^{(m)} = (v_0)^2/m\omega\sqrt{\Phi}. \tag{76}$$

(ii) Self-similar (statistical fractal) fluctuations. In this case the correlation function of fluctuations has a long tail of the negative power-law type

$$\langle \Delta v(t_1)\Delta v(t_2)\rangle = \Phi(|t_1-t_2|) = \mathcal{M}|t_1-t_2|^{-\sigma},$$
$$\mathcal{M}>0,\ 1>\sigma>0, \tag{77}$$

where $1>\sigma>0$ is a fractal exponent between zero and unity. The amplitude factors and the localization length are given by

$$T^{(m)}(x) = \exp\left[-\frac{m^2\omega^2\mathcal{M}}{(1-\sigma)(2-\sigma)(v_0)^{4-\sigma}}\,x^{2-\sigma}\right], \tag{78}$$

$$\lambda_d^{(m)} = \left[\frac{(1-\sigma)(2-\sigma)(v_0)^{4-\sigma}}{m^2\omega^2\mathcal{M}}\right]^{1/(2-\sigma)}. \tag{79}$$

(iii) Markovian fluctuations. For Markovian fluctuations the correlation function of the velocity decreases exponentially with increasing time difference (t_1-t_2):

$$\langle \Delta v(t_1)\Delta v(t_2)\rangle = \Phi(|t_1-t_2|)$$
$$= \langle[\Delta v(0)]^2\rangle \exp[-\Omega|t_1-t_2|], \tag{80}$$

where Ω is the decay rate of the velocity fluctuations. We have

$$T^{(m)}(x) = \exp\left\{-\frac{m^2\omega^2\langle[\Delta v(0)]^2\rangle}{(v_0)^2\Omega^2}\times\left[\frac{\Omega x}{v_0}-1+\exp\left(-\frac{\Omega x}{v_0}\right)\right]\right\}. \tag{81}$$

In this case the damping length cannot be evaluated analytically in the general case. We distinguish two subcategories.

(a) Slow fluctuations $(\Omega\sim 0)$. We have

$$T^{(m)}(x) = \exp\left[-\frac{m^2\omega^2\langle[\Delta v(0)]^2\rangle}{2(v_0)^4}\,x^2\right], \quad \Omega\sim 0 \tag{82}$$

$$\lambda_d^{(m)} = (v_0)^2/m\omega\sqrt{\langle[\Delta v(0)]^2\rangle}, \quad \Omega\sim 0. \tag{83}$$

(b) Fast fluctuations $(\Omega\gg 0)$. We obtain

$$T^{(m)}(x) = \exp\left[-\frac{m^2\omega^2\langle[\Delta v(0)]^2\rangle}{\Omega(v_0)^3}\,x\right], \quad \Omega\gg 0 \tag{84}$$

$$\lambda_d^{(m)} = \frac{\Omega(v_0)^3}{m^2\omega^2\langle[\Delta v(0)]^2\rangle}, \quad \Omega\gg 0. \tag{85}$$

(iv) Independent fluctuations. In this case the fluctuations of speed are independent and the correlation function is represented by a δ function

$$\langle \Delta v(t_1)\Delta v(t_2)\rangle = \Phi(|t_1-t_2|) = 2D_{\mathrm{eff}}\delta(|t_1-t_2|), \tag{86}$$

where D_{eff} is an effective diffusion coefficient. In this case the amplitude factors have an exponential shape

$$T^{(m)}(x) = \exp\left[-\frac{2m^2\omega^2 D_{\mathrm{eff}}}{(v_0)^3}\,x\right], \tag{87}$$

$$\lambda_d^{(m)} = \frac{(v_0)^3}{m^2\omega^2 D_{\mathrm{eff}}}. \tag{88}$$

Equations (86) and (87) are a particular case of Eqs. (80) and (81) derived for Markovian fluctuations. Equation (86) can be derived from Eq. (80) by assuming that the rate Ω of fluctuation regression tends to infinity and the dispersion of speed fluctuation $\langle[\Delta v(0)]^2\rangle$ tends to zero subject to the constraint that their product remains constant:

$$\Omega\to\infty, \quad \langle[\Delta v(0)]^2\rangle\to 0$$
$$\text{with } D_{\mathrm{eff}} = \tfrac{1}{2}\Omega\langle[\Delta v(0)]^2\rangle = \text{const}. \tag{89}$$

The limit (89) is of the diffusion type.

The above analysis shows that the Anderson localization of a reaction-convection chemical pattern is influenced by the type of stochastic process describing the dynamics of velocity fluctuations. The localization effect increases with the memory of the stochastic process. For infinite memory the damping factors are Gaussian. For finite, self-similar long memory the damping of the chemical patterns is less pronounced and is described by a stretched exponential. For Markovian processes with short memory the localization of chemical patterns is even slower and the tails of the attenuation factors are exponential. Finally, for independent random processes without memory the localization is exponential for any distance, short or long. Further the analysis shows that there is a close relation between localization and the self-similar features of the fluctuations: For the system studied long memory corresponds to self-similarity and as the strength of the memory effect increases, the efficiency of the localization increases.

To illustrate this effect we have performed a numerical study of localization in a reaction convection system of the Sel'kov type [16]. The Sel'kov model is given by the reaction scheme

$$A \underset{k_{-1}}{\overset{k_{+}}{\rightleftarrows}} X, \quad X+2Y \underset{k_{-2}}{\overset{k_{+2}}{\rightleftarrows}} 3Y, \quad Y \underset{k_{-3}}{\overset{k_{+3}}{\rightleftarrows}} B, \tag{90}$$

where A and B are stable species with concentrations kept constant by an interaction with large external reservoirs and X and Y are reaction intermediates with concentrations variable in time. In a homogeneous system the reaction mechanism (90) may display a stable limit cycle for certain values of the rate coefficients and of the concentrations of stable

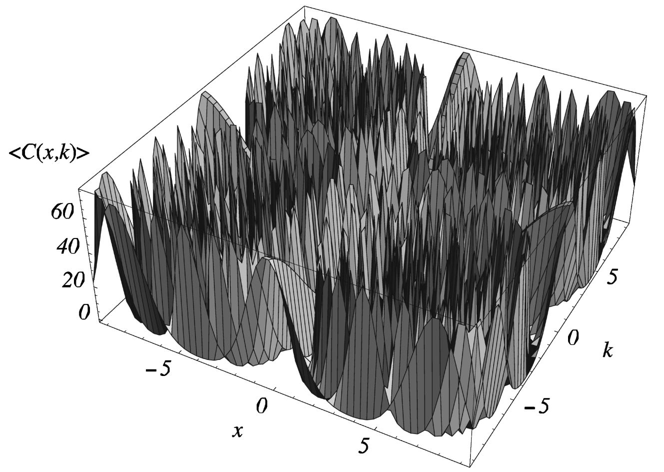

FIG. 1. Space and wave-number dependence of the stationary concentration field of the active intermediate X for the Sel'kov model operated in an infinite reaction tube. The concentration profile is stationary, periodic both in position and in wave number k, and is invariant to the permutation of x and k.

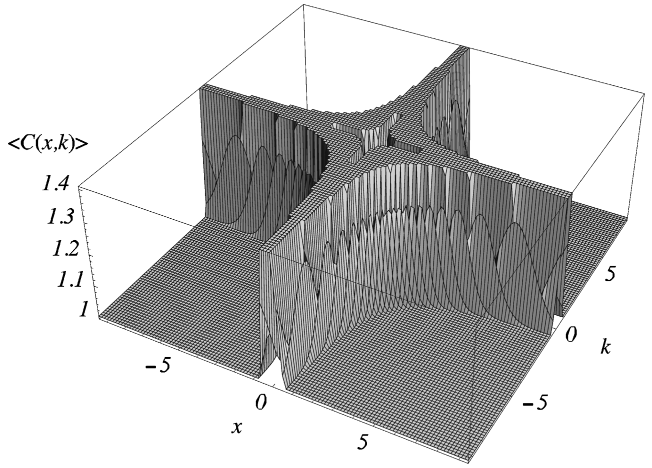

FIG. 2. Space and wave-number dependence of the ensemble average of the concentration of the active intermediate X for the Sel'kov model operated in an infinite reaction tube and subject to random velocity fluctuations with infinite memory. The localization is very strong and, although the different random realizations of the concentration profile are time dependent, the ensemble average is stationary and invariant to the permutation of x and k.

species A and B. The kinetic equations of the Sel'kov model (90) are integrated numerically. For large times the process is approaching a stable limit cycle and the time variation of X and Y becomes periodic. The periodic motion of X is analytically continued for any values of the time axis, from $-\infty$ to $+\infty$, and the corresponding function are subject to Fourier analysis; we have computed the phases and the amplitudes of the first ten harmonics. By using the general analysis developed in this article the Fourier components are used to compute the periodic stationary patterns that emerge for long times in a reaction tube characterized by different flow rates. To avoid the complications generated by the nonperiodic behavior of the concentration profiles at the beginning of the reaction tube we have assumed that the reaction tube has an infinite length and that the chemicals are introduced into the system either at $x_0 \rightarrow -\infty$ or at $x_0 \rightarrow +\infty$. According to the dispersion relation (51), different propagation speeds ν_0 along the reaction tube correspond to different values of the wave number $k = \nu_0/\omega$. The wave number, just like the coordinate x along the reaction tube, can take any real value from $-\infty$ to $+\infty$. A positive value of $k = \nu_0/\omega$ corresponds to a positive value of ν_0 and in this case the reagents are introduced into the system at $x_0 \rightarrow -\infty$; similarly, a negative value of $k = \nu_0/\omega$ corresponds to a negative propagation velocity and in this case the chemicals are fed at $x_0 \rightarrow +\infty$. For an infinite system without fluctuations the concentration field is a double periodic function in both x and k. Figure 1 displays a three dimensional representation of the concentration of the chemical species X as a function of position and the wave vector. Notice the perfect symmetry of the field with respect to the permutation of variables x and k; this symmetry is a consequence of the structure of the Fourier representation (50) of the concentration field.

In addition, we have investigated the effect of different types of noise on the dependence of the concentration field. Figure 2 displays the localization effect due to stochastic fluctuations with infinite memory. In this case the localization effect is very strong; it is interesting that in spite of the localization in space, for infinite memory the concentration field is still symmetric with respect to the permutation of x and k. For long but finite memory the fluctuations of the random component of the velocity are self-similar and the localization effect is still strong; however, in this case the localization effect acts in different ways along the axes, respectively (Fig. 3). For both Markovian and independent processes the localization is weak. The results of our numerical computations are practically identical in these two cases (see Fig. 4); we cannot identify any differences because of the limited number of harmonics used in our computations. In these two cases the symmetry of the localized field with respect to the permutation of x and k is restored.

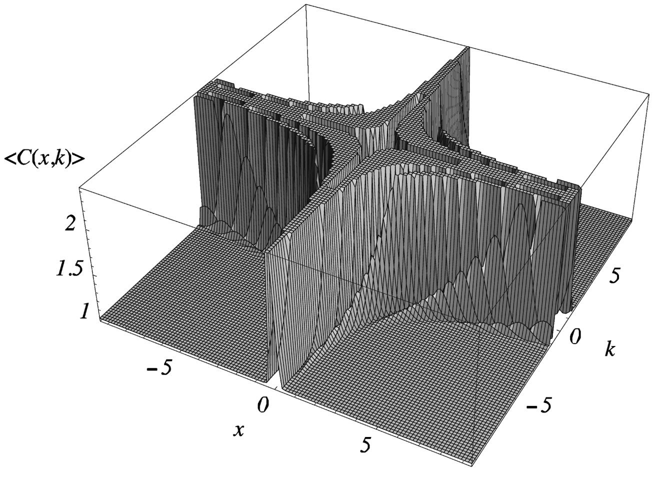

FIG. 3. Space and wave-number dependence of the ensemble average of the concentration of the active intermediate X for the Sel'kov model operated in an infinite reaction tube and subject to random velocity fluctuations with long but finite memory characterized by a fractal exponent $H = 1.2$. The localization is still strong and the ensemble average is also stationary, but it is no longer invariant to the permutation of x and k.

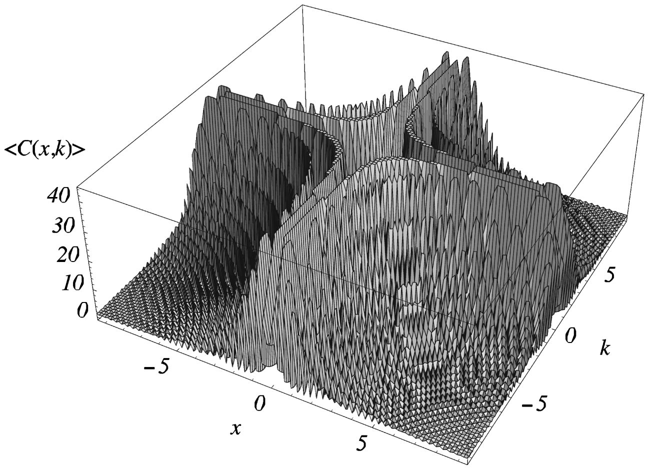

FIG. 4. Space and wave-number dependence of the ensemble average of the concentration of the active intermediate X for the Sel'kov model operated in an infinite reaction tube and subject to random velocity fluctuations with short memory (Markovian) or without memory. The localization is weak; the ensemble average is stationary and invariant to the permutation of x and k.

VII. DISCUSSION

The main results obtained in this article are the following.

(i) A general approach for analyzing the behavior of chemical waves and patterns in a random medium with small fluctuations has been developed, based on the method of phase linearization. The approach leads to a cumulant series expansion expressing the contributions of environmental fluctuations to the moments of the concentration fields.

(ii) It has been shown that the environmental disorder may lead to Anderson localization.

(iii) The general approach developed in the article has been applied for the evaluation of the average concentration fields in the case of a chemical oscillator operated in an one-dimensional ideal tubular reactor.

(iv) If the time evolution of a chemical oscillator operated in a homogeneous, well-stirred reactor is approximated for a finite period of time by a stable limit cycle, then the same process operated in a reaction tube with constant velocity displays periodicity in space for a finite characteristic length. Theoretically, if the chemical oscillator operated in a homogeneous reactor evolves towards a time-dependent normal regime corresponding to a stable limit cycle, then the same process operated in a reaction tube with constant velocity tends towards a stationary regime characterized by chemical patterns periodic in space. Although this statement is mathematically correct, it is very hard to find a real chemical system for which it actually occurs. In the first place, even in a homogeneous system, a stable limit cycle cannot be maintained forever. In the case of the Sel'kov model considered in this paper [Eq. (90)] the limit cycle may occur only if the concentrations of stable species A and B are kept constant. In a closed homogeneous system the time invariance of A and B can be accomplished for a finite time period by introducing initially a large excess of these two reagents in the system. As the process goes on, eventually the concentrations of A and B vary in time, resulting in the destruction of the limit cycle. A similar phenomenon takes place in an ideal reaction tube. If in the input flux the reagents A and B are in large excess, then for small to moderately large distances from the entrance in the reactor their concentrations are practically constant and the concentrations of X and Y are approaching a periodic regime corresponding to a limit cycle. For large values of the space coordinate, however, the concentrations of A and B are no longer constant, the oscillations in X and Y are damped, and eventually the limit cycle is destroyed.

(v) If the mainstream velocity is subject to a small random perturbation described by a stationary Gaussian random process then the ensemble average of stationary concentration fields displays the phenomenon of localization. The stationary chemical patterns are no longer periodic, but display damped oscillations along the reaction tube. The strength of localization depends on the memory of the velocity fluctuations and increases with increasing memory effects.

The results presented in this article have been derived by using a method of phase linearization that is less restrictive than the linearization of the kinetic equations. Within our approach the underlying deterministic kinetic equations are nonlinear and no attempt has been made to linearize them. The assumption made is that the main contribution of the velocity fluctuations of the phases of different chemicals is of first order with respect to the variation $\Delta\nu$ of velocity. Our technique is a stochastic analog of the Bogoliubov-Mitropolskii technique of harmonic linearization [8]. Our analysis shows that even the slightest fluctuations of velocity lead to the localization of the chemical patterns.

The example used to illustrate our approach has been analyzed by assuming the validity of the model on an ideal tubular reactor. Although very popular in the literature of chemical engineering, this model gives only an approximate description of the real systems. For laminar flows there are distinct velocity variations in the radial direction (normal to the flow). In such a case the flow cannot be described as uniform in the radial direction, but may be approximated by a plug flow on which a (Taylor) axial dispersion is superimposed. On the other extreme of strong turbulence, the longitudinal turbulent dispersion may have an important contribution to the mass transport. Despite these limitations, we believe that the application of our approach to the case of ideal tubular reactors is more than a simple academic exercise: A detailed theoretical analysis is possible yet, despite its simplicity, it leads to Anderson localization.

An interesting problem is related to the possible experimental identification of the localization of reaction-convection chemical patterns. The analysis presented in this paper is based on the assumption that the velocity fluctuations along the reaction tube are space independent. Such an assumption holds for relatively slow chemical processes for which the chemical time scales are at least an order of magnitude smaller than the mechanical time scale characteristic of the propagation of the velocity fluctuations along the reaction tube. We suggest an experimental installation of a computer-controlled pump coupled to a tubular reactor and repeated measurement of the concentration profiles along the reaction tube corresponding to different realizations of the fluctuations of the speed generated by the computer. If the number of experiments is large enough we predict that the ensemble average of the concentration profiles evaluated from the measured data displays localization. Because of the limitations of the model of ideal tubular reactors, we do not expect quantitative agreement with the theory; nevertheless, we predict localization.

At least in principle, the general approach suggested in this article can be applied to any structured chemical system, involving various phenomena such as molecular or turbulent diffusion, mainstream hydrodynamic flow, and nonlinear chemical reactions. However, the application presented is limited to the study of convection-reaction systems. The mathematical structure of these systems makes possible a detailed analytical treatment of the problem of Anderson localization. The majority of the physicochemical literature dealing with inhomogeneous nonlinear chemical systems, however, consider only reaction-diffusion systems. The so-called chemical waves are completely different from the periodic patterns considered in this article. A chemical wave is generated by the competition between a chemical process and molecular diffusion. Because of this, the velocity v of propagation of a chemical wave increases not only with increasing diffusion coefficient D but also with increasing reaction rate R

$$v \sim \sqrt{DR}. \tag{91}$$

Therefore, a perturbation of a nonlinear reaction diffusion system will spread quite fast and the corresponding propagation rate is process dependent. For such a system the normal behavior corresponds to the generation of nonstationary phase waves rather than the stationary patterns characteristic of reaction convection systems discussed in this article. However, even for a pure reaction-diffusion system a stationary pattern can be observed under certain conditions. It has been shown on the basis of local bifurcation theory that standing waves may be found in systems with at least three variables and unequal diffusion coefficients (long-range coupling [17–19]). The type of stationary pattern discussed in this paper is different; it is generated by the balance between the generation and consumption of the chemicals and the convective transport. We expect that our description is fairly correct for systems for which the convective transport outweighs the contribution of molecular and turbulent diffusive transport.

An interesting problem is related to the interpretation of the relations between the memory of the speed fluctuations and the localization effect. The localization displayed by the ensemble average of the concentration profile is due to the destructive interference of the different realizations of the relative fluctuations of the concentration fields that make up the ensemble. As the strength of fluctuations increases with the increase of the memory effects it follows that for long memory the destructive interference leads to stronger damping, which is consistent with the results of our calculations.

Concerning future research, five general problems arise. The first problem is related to the possibilities of generalizing our approach for processes in which diffusion cannot be neglected. In view of the general considerations about reaction-diffusion systems mentioned above, we normally expect that in this case stationary patterns do not exist; however, the Anderson localization can be present also in the case of nonstationary fields. The second problem is of the interaction between the internal thermal fluctuations of the system and the external fluctuations of the mainstream velocity. This type of problem can be dealt with by using the theory of processes with dynamical disorder [20]. To solve it we should develop a Fourier analysis of fluctuating concentration fields and suitable methods of dynamical averaging. The third problem is the investigation of the influence of environmental fluctuations in systems displaying quasiperiodic or chaotic behavior [21]. The fourth problem is related to the generalization of our approach for the case when the moments of fluctuation are infinite and the stochastic process obeys Lévy statistics; for this type of system the tails of the probability distributions display self-similarity rather than the correlation functions. The generalization of our approach for these classes of systems is not limited to the reaction-convection processes considered in this article, but is of general interest in connection with the study of wave propagation in random media. For these systems the path averaging technique developed in this article should be combined with the Shlesinger-Hughes renormalization approach [22]. The fifth problem is the application of the theory for the more complicated case of a chemical oscillation in a heterogeneous system displaying phase diffusion [23].

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