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FORMATION OF HETEROGENEOUS REACTION REGIMES UNDER THE ACTION OF MULTIPLICATIVE NOISE

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It is shown that transitions from the diffusion regime to the kinetic regime are possible when the fluctuations of the heat transfer from the zone of an exothermic reaction exceed a certain critical value, and the diffusion regime of the reaction can be suppressed when they exceed a second, higher level.

The occurrence of fluctuations of the properties of nonlinear dynamical and physicochemical systems and of the parameters of external fields interacting with those systems can radically influence the behavior of the systems. The systems are no longer described by deterministic equations in this case, but by stochastic equations of the Langevin type with the inclusion of additive and multiplicative noise. The existence of the latter cannot only alter the characteristics of the steady-state regimes in the quantitative respect, but also lead to a qualitative reorganization of these regimes, along with their stability domains and the condition underlying their occurrence (see, e.g., [1]).

The action of "white" noise (delta-correlated Gaussian stochastic processes) on the formation of the regimes of lumped-parameter physicochemical systems was first investigated [2-4] by analyzing the steady-state solutions of the Fokker–Planck equations corresponding to the stochastic equations for these systems. The influence of "colored" noise, i.e., situations in which the correlation time of the stochastic processes is commensurate with the time scale of the mean characteristics of the system, has been investigated [5-7]. Some of the authors [4-7] have reported the observation of transitions to bistable behavior. A certain classification of such transitions and a survey of research in the indicated direction may be found in [8]. Analogous phenomena in distributed systems appear to have been treated for the first time [9] on the basis of an analog of the Ginzburg–Landau equation in the theory of second-order phase transitions.

In the present article we investigate the influence of fluctuations of the heat- and mass-transfer coefficients on the process of a heterogeneous exothermic reaction (combustion) described by the system of nonlinear equations [10]

$$\begin{gathered}\varepsilon dc/dt = \beta(c_0 - c) - k(T)c,\\ c_p dT/dt = Qk(T)c - \alpha(T - T_0),\\ k(T) = z\exp(-E/RT).\end{gathered} \qquad (1)$$

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A structurally similar system of equations can be used to describe certain other processes of practical importance, e.g., the reaction process in an ideal mixing reactor [10]. The parameter ε is usually small, making it possible to neglect the left-hand side of the first equation (1), to express c in the equation as a function of T, and to derive the single equation

$$c_p \frac{dT}{dt} = \frac{Qc_0\beta k(T)}{\beta + k(T)} - \alpha (T - T_0). \tag{2}$$

However, this equation is usually unsuitable for analysis when α and β are random time functions. Consequently, the procedure for the adiabatic elimination of one of the unknown functions from Eqs. (1) must be devised by the general method proposed in [11, 12]. We set

$$\alpha(t) = \langle \alpha \rangle + \alpha'(t), \quad \beta(t) = \langle \beta \rangle + \beta'(t), \tag{3}$$

where $\langle\alpha\rangle$ and $\langle\beta\rangle$ are constants, and $\alpha'(t)$ and $\beta'(t)$ are stochastic processes with zero means. We assume for definiteness and for simplification that the correlation time of the indicated stochastic processes is very small, i.e., that they can be regarded approximately as white noise. The following representation is admissible in this case [11, 12]:

$$\begin{gathered} \frac{\alpha'(\tau)}{\langle \alpha \rangle} = \sqrt{2D_1}\frac{dw_1}{d\tau} + \sqrt{2D_2}\frac{dw_2}{d\tau}, \\ \frac{\beta'(\tau)}{\langle \beta \rangle} = \sqrt{2D_3}\frac{dw_1}{d\tau} = \sqrt{2D_4}\frac{dw_2}{d\tau}, \end{gathered} \tag{4}$$

where $w_j(\tau)$ $(j = 1, 2)$ are independent Wiener stochastic processes, for which $\langle w_j\rangle = 0$, $\langle w_j^2\rangle = \tau$, $\langle w_1 w_2\rangle = 0$. The introduction of two such processes in the form (4) enables us to describe the possible correlation between $\alpha'(t)$ and $\beta'(t)$; if the latter do not correlate, it is required to set $D_2 = D_3 = 0$. Here τ is the dimensionless time.

As in the standard method of "expansion of the exponential" [10], we introduce the dimensionless variables and parameters

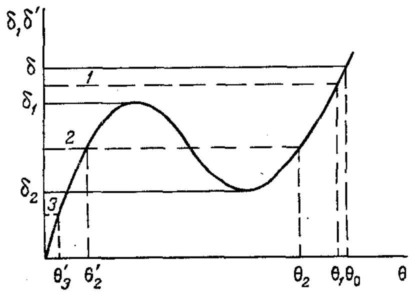
$$\begin{gathered} \theta = \frac{T - T_0}{\sigma T_0}, \quad x = \frac{c_0 - c}{c_0}, \quad \tau = \frac{\langle \alpha \rangle}{c_p} t, \quad \sigma = \frac{RT_0}{E}, \\ \mu = \frac{z}{\langle \beta \rangle}\exp\left(-\frac{1}{\sigma}\right), \quad \delta = \frac{c_0 Q z}{\sigma \langle \alpha \rangle T_0}\exp\left(-\frac{1}{\sigma}\right), \\ k(T) = z\exp\left(-\frac{1}{\sigma}\right)\exp\frac{\theta}{1+\sigma\theta}, \quad \gamma = \frac{\langle \beta \rangle c_p}{\langle \alpha \rangle \varepsilon}. \end{gathered} \tag{5}$$

Equations (1) can be written in the standard form for stochastic equations in the variables (5) with allowance for Eqs. (3) and (4):

$$\begin{gathered} dx = \gamma\left[-x + \mu(1-x)\exp\frac{\theta}{1+\sigma\theta}\right]d\tau - \gamma x\left(\sqrt{2D_1}\,dw_1 + \sqrt{2D_2}\,dw_2\right), \\ d\theta = \left[\delta(1-x)\exp\frac{\theta}{1+\sigma\theta} - \theta\right]d\tau - \theta\left(\sqrt{2D_3}\,dw_1 + \sqrt{2D_4}\,dw_2\right). \end{gathered} \tag{6}$$

Respecting the physical significance of the investigated problem, we must interpret Eqs. (6) in the sense of Stratonovich [1, 11]. These stochastic differential equations can then be set in correspondence with the Fokker–Planck equation:

$$\begin{aligned} \frac{\partial f}{\partial \tau} = &-\frac{\partial}{\partial x}\left\{\left[\gamma^2(D_3 + D_4)x + \gamma\left(-x + \mu(1-x)\exp\frac{\theta}{1+\sigma\theta}\right)\right]f\right\} - \\ &-\frac{\partial}{\partial \theta}\left\{\left[(D_1 + D_2 - 1)\theta + \delta(1-x)\exp\frac{\theta}{1+\sigma\theta}\right]f\right\} + \\ &+\gamma^2\frac{\partial^2}{\partial x^2}\left[(D_3 + D_4)x^2 f\right] + \frac{\partial^2}{\partial \theta^2}\left[(D_1 + D_2)\theta^2 f\right] + \\ &+2\gamma\frac{\partial^2}{\partial x \partial \theta}\left[\left(\sqrt{D_1 D_3} + \sqrt{D_2 D_4}\right)x\theta f\right] \end{aligned} \tag{7}$$



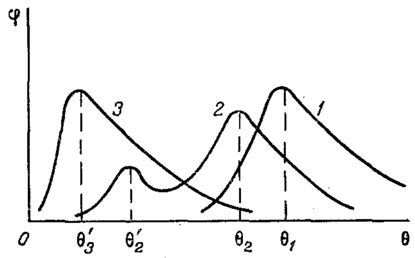


Fig. 1 Fig. 2

Fig. 1. Graphical solution of Eqs. (14) and (15).

Fig. 2. Qualitative behavior of the probability density function under steady-state conditions at different noise levels.

[when Eqs. (6) are interpreted in the sense of Itô, it is required to drop terms containing D_j in the components of Eq. (7) that describe "convective" entrainment]. Here $f = f(\tau, x, \theta)$ is the probability density function in the plane of the variables x and θ.

If the relaxation time τ_x of the reagent concentration is much smaller than such a time τ_θ for the temperature in the reaction zone (as is customary, e.g., for heterogeneous combustion processes), it is possible to eliminate the variable x adiabatically. This is accomplished formally by transforming as $\gamma \to \infty$ to the new density function $\phi(\tau, \theta)$, which represents the results of averaging $f(\tau, x, \theta)$ over time intervals $\Delta\tau$ that satisfy the inequalities $\tau_x \ll \Delta\tau \ll \tau_\theta$. Such a transformation can be made in principle, by the machinery of projection operators [12], or, in general, by application of the familiar asymptotic method of multiple scales. The specific implementation of this program in application to the investigated system poses a rather complex independent problem. Consequently, looking at the physical side of the issue, we assume here that only the quantity α in Eqs. (1) fluctuates, i.e., the indicated adiabatic elimination can be achieved by simply transforming from Eqs. (1) to the single nonlinear equation (2). In this case $D_1 = D \neq 0$, $D_2 = D_3 = D_4 = 0$, and the Langevin stochastic equation used in place of (6) has the following form in the variables (5):

$$d\theta = \left[\delta\left(\mu + \exp\frac{-\theta}{1+\sigma\theta}\right)^{-1} - \theta\right]d\tau - \theta\sqrt{2D}\,dw \tag{8}$$

and it can be associated (in the sense of Stratonovich) with the Fokker–Planck equation

$$\frac{\partial\varphi}{\partial\tau} = -\frac{\partial}{\partial\theta}\left\{\left[\delta\left(\mu + \exp\frac{-\theta}{1+\sigma\theta}\right)^{-1} - (1-D)\,\theta\right]\varphi\right\} + D\frac{\partial^2}{\partial\theta^2}(\theta^2\varphi). \tag{9}$$

We write the solution of the steady-state counterpart of Eq. (9). Integrating it once under the obvious condition $d\phi/d\theta \to 0$ as $\theta \to \infty$, we have

$$\frac{d\varphi}{\partial\theta} = \left[\frac{\delta}{D\theta^2}\left(\mu + \exp\frac{-\theta}{1+\sigma\theta}\right)^{-1} - \frac{1+D}{D\theta}\right]\varphi. \tag{10}$$

The solution (10) can be written in the form

$$\varphi = C\theta^{-1-1/D}\exp\left(\frac{\delta F}{D}\right), \quad \frac{dF}{d\theta} = \frac{1}{\theta^2}\left(\mu + \exp\frac{-\theta}{1+\sigma\theta}\right)^{-1}, \tag{11}$$

where F(θ) is interpreted as an indefinite integral, i.e., the inverse (antiderivative) of its derivative, and C is a constant evaluated on the basis of the normalization condition. Unfortunately, F(θ) cannot be expressed in terms of known functions, but for sufficiently small and sufficiently large values of θ we obtain

$$F(\theta) \sim -\frac{1}{(1+\mu)\,\theta}, \ \theta \ll 1; \quad F(\theta) \sim -\frac{1}{\mu\theta}, \ \theta \gg 1, \tag{12}$$

from which it follows that $\phi(\theta)$ vanishes in the limit $\theta \to 0$. It is also readily shown that the integral of $\phi(\theta)$ with respect to dθ is finite in the interval $(0, \infty)$.

In the general case, F(θ) can be written formally as

$$F = -\frac{1}{(1+\mu)\theta} + \sum_{m=1}^{\infty} \frac{(-1)^m}{(1+\mu)^{m+1}} \int \left[\sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \left(\frac{\theta}{1+\sigma\theta} \right)^n \right]^m d\theta. \tag{13}$$

Setting aside the problem of the actual form of $\varphi(\theta)$ and evaluating the constant C, we find the extremum points of this function. We obtain the following equation for them from Eq. (10):

$$\delta' = \frac{\delta}{1+D} = \theta \left(\mu + \exp \frac{-\theta}{1+\sigma\theta} \right) \equiv g(\theta;\ \mu,\ \sigma). \tag{14}$$

Together with Eq. (14), we also analyze the analogous equation

$$\delta = \theta \left(\mu + \exp \frac{-\theta}{1+\sigma\theta} \right) \equiv g(\theta;\ \mu,\ \sigma), \tag{15}$$

which determines the dimensionless temperature in the steady states of a heterogeneous exothermic reaction in the absence of fluctuations. The parameter σ is usually small; the solutions (14) and (15) have been investigated in detail for $\sigma = 0$ [10]. If $\mu < \mu_*(\sigma)$ $(\mu_*(0) = e^{-2})$, the function $g(\theta;\ \mu,\ \sigma)$ is nonmonotonic and has the form shown in Fig. 1. The behavior of the reaction can differ qualitatively in this case, depending on the quantity δ (Fig. 1): For $\delta > \delta_1$, a single stable regime with $\theta = \theta_0$ exists, in which the reaction rate is limited by the rate of diffusion influx of the reagent and for $\delta < \delta_2$ a single regime occurs, which is limited by kinetic factors. In the interval $\delta_2 < \delta < \delta_1$, diffusion and kinetic stable regimes coexist [the regime corresponding to the descending branch of $g(\theta;\ \mu,\ \sigma)$ is unstable]. The critical values of the parameter δ_1 and δ_2, of course, depend on μ and σ.

If heat-transfer fluctuations take place $(D \neq 0)$, the stationary density function $\phi(\theta)$ of the realization of different values of θ must be analyzed instead of a definite value of θ characterizing the steady state within the framework of the deterministic model. It is seen at once that the presence of external noise can indeed result in a radical rearrangement of the physical pattern of the process. Suppose, e.g., that $\delta > \delta_1$, so that the diffusion regime $\theta = \theta_0$ shown in Fig. 1 occurs under deterministic conditions. If the quantity D characterizing the level of the fluctuations is not too great $(\delta' > \delta_1$, i.e., $D < \delta/\delta_1 - 1)$, it is still possible to have a single diffusion regime described by a function $\phi(\theta)$ of the type represented by curve 1 in Fig. 2; the value of the temperature in the reaction zone obeys the inequality $\theta_1 < \delta_0$ in this case (see the straight line 1 in Fig. 1). If $\delta/\delta_2 - 1 > D > \delta/\delta_1 - 1$, the transition is made to a bistable situation similar to that in [4-7], where the function $\phi(\theta)$ has two maxima, which correspond to the diffusion regime and the kinetic regime with respective temperatures $\theta_2 < \theta_1$ and θ_2' (situation 2 in Figs. 1 and 2). Finally, if $D > \theta/\theta_2 - 1$, the maximum of $\phi(\theta)$ corresponding to the diffusion regime vanishes altogether, and only the kinetic regime remains with a temperature $\theta_3' < \theta_2'$ (curves 3 in Figs. 1 and 2). Analogously, if two stable regimes are possible under deterministic conditions $(\delta_2 < \delta < \delta_1)$, fluctuations can eliminate the diffusion regime. On the whole, the temperature of the reaction zone decreases as D is increased.

Thus, the presence of external noise leads, first, to quantitative variations of the steady-state characteristics with the onset of statistical scatter and, second, to a qualitative modification of the behavior of the system. The above-described pattern is completely consistent with the results of other studies of the influence of noise on nonlinear systems [8]. However, a conceptually new phenomenon emerges in the above-mentioned possibility of actual extinction of the reaction, i.e., a transition from the diffusion regime to the kinetic regime when the fluctuations exceed a definite critical level. The occurrence of such a transition indicates that the application of the classical deterministic theory of heterogeneous exothermic reactions [10] to systems subjected to external noise effects can induce qualitative as well as quantitative errors. This conclusions is also valid hypothetically in the situation where the fluctuations of the heat-transfer coefficient α are accompanied by fluctuations of a second regime parameter: the mass influx coefficient β of the reagent, and additive noise sets in together with multiplicative noise as a result of fluctuations of the external temperature T_0 and the unperturbed concentration c_0. The analysis of these effects requires further investigation along the lines set forth in this article.

NOTATION

C, normalization constant; c, concentration; c_p, specific heat; D_j, diffusion coefficients in the plane of the dimensionless temperature and the dimensionless concentration; E, activation energy; F, function defined in Eqs. (12) and (13); f, probability density function; g, function in Eqs. (14) and (15); k, reaction rate; Q, heat of reaction; R, gas constant; T, temperature; t, time; w_j, Wiener processes; x, dimensionless concentration; z, coefficient of the exponential in Eq. (1); α, heat-transfer coefficient; β, mass influx coefficient of reagent; γ, δ, μ, σ, parameters defined in Eq. (5); ε, small parameter in Eq. (1); θ, dimensionless temperature; τ, dimensionless time; ϕ, probability density function.

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RADIATION HEAT TRANSFER IN TWO-PHASE MEDIA

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The state of the art of approximate and numerical methods of the theory of radiation heat transfer is analyzed. The principles for producing engineering methods of computing the radiation heat-transfer characteristics in power plants are examined.

Investigations of radiation heat transfer in two-phase media play an important part in many areas of physics and modern engineering. Their value has recently grown considerably in connection with the rapid development of new techniques and intensification of technological processes associated with the significant increase in the power of energy installations. This results in a need for a more correct solution of radiation heat-transfer problems. The development of methods of the theory of radiation heat transfer should, in our opinion, proceed in two directions, the development of well-founded approximate methods and effective numerical algorithms. If the first methods are needed to carry out correct estimates of the radiation heat-transfer phenomena, to study complex thermophysical processes, then the second is for the production of effective engineering methods and to give a foundation for the approximate methods being developed. Taking into account such important physical phenomena for radiation heat transfer as multiple scattering, selectivity of absorption, thermodynamic nonequilibrium, polydispersity, inhomogeneity and geometry of the emitting volume, etc., is still performed insufficiently correctly in the literature. Even more so, if we speak of a one-time accounting of these phenomena. The solution of such questions would approximate physical models selected to real objects. Moreover, it is necessary to give a physically rigorous foundation of the effective quantities used in radiation heat-transfer practice (effective temperature of the working volume, effective emissivity of the heat carrier, coefficient of thermal efficiency of the screens, etc.). It should be noted that the solution of such problems is also of extreme importance for plasma physics, problems

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