Investigation of the Nanoparticles Motion Modes within the Framework of Stochastic System

O.V. Yushchenko*, A.Yu. Badalyan

Sumy State University, 2, Rimsky-Korsakov Str., 40007 Sumy, Ukraine

On the basis of a stochastic system of equations, describing the behavior of the average velocity of nanoparticles, the external field and the internal energy, a synergetic model, which allows in a self-consistent manner to present the modes of the suspended nanoparticles motion, was constructed. Considering the correlation between the times of change of the degrees of freedom the Fokker-Planck equation was obtained, and the corresponding Langevin equation was found. Phase diagram of the system was built and the dependence of steady-state average velocity on the external conditions was found. Within the framework of the phase-plane method the kinetics of the transition between the modes of the nanoparticles motion was investigated.

Keywords: Self-organization, Fokker-Planck equation, Langevin equation, Phase-plane method.

PACS numbers: 05.40.Jc, 02.50. – r

1. INTRODUCTION

Control and governing of nanoparticles motion are of a great interest in connection with the development of nanotechnologies. Solution of such a problem can be applied to a wide range of technological problems including nano- and microfluidic problems [1], to the aspects of creation of the newest sensors [2], as well as to the development of nanomotors and reactor devices [3-8]. Delivery of particles to a certain place where they are necessary, for example, for targeted drug delivery or in industrial reactors is the main factor in this case.

It is known that for some existing reactors they use catalytic particles whose size is determined by acceptable technical conditions when flux of reactants passes through a catalyst layer [9]. In this case, high activity necessary for catalysts is achieved due to the increase in the surface area of active phase (from 25 to 500 m² on 1 ml) that becomes possible only for very small catalytic particles (of the order of 50 nm) [10].

As a result, the control problem of motion modes of active nanoparticles is a promising one at present [11-16]. Usage of different radiation [11, 12] is the simplest mechanism here. For example, suspended particles which are present in sufficiently dense liquid flux can be controlled by time-dependent radiation. Moreover, analyzing the concentration distribution of suspended particles, one can judge the intensity of incident radiation, and as a result, formation of a new class of liquid-based radiation sensors is possible.

Since the matter is suspended particles, it is reasonable to address the description of Brownian motion [11, 12, 17]. In spite of the fact that theory of such motion was studied by A. Einstein in the beginning of the last century, some observed effects are explained only now based on the investigation of the so-called "hot" Brownian motion [11-13]. It differs from the usual Brownian motion by the fact that nanoparticles (gold nanoparticles were used in the works [11, 12]) heated by a focused laser radiation have the external energy storage which later is transformed into mechanical energy.

As a result, nanoparticle motion is conditioned not only by spontaneous impacts of molecules of surrounded liquid, but also by the transformation of existing external energy storage into motion energy.

Obviously that the above described systems are open and far from the thermodynamic equilibrium, therefore, they can support own order only in the case when the processes which define their behavior are non-linear.

As a result, the aim of the present work is the modeling of motion modes of suspended nanoparticles within the framework of the "hot" Brownian motion model [11, 12, 17].

2. SYNERGETIC SYSTEM OF EQUATIONS

According to the work [17], the base of such description is the synergetic system of equations determining self-consistent behavior of three degrees of freedom:

- the order parameter which is reduced to the average velocity of nanoparticles motion v;
- the conjugate field which represents the strength of the external field h (in the case of the chemotaxis phenomenon [15], when nanoparticles move directly according to the concentration distribution of chemical reactants, the given parameter corresponds to the concentration gradient of the corresponding chemical substances);
- the control parameter which can be associated with the internal energy ε of particles.

As a result, the problem is reduced to the expression of the rates of the mentioned degrees of freedom through their values v, h, and ε. Since only one preferential direction exists for rectilinear motion of nanoparticles, then it is appropriate to analyze later the one-dimensional case. Moreover, it is known from the works [11, 12, 17-19] that several motion modes are typical for the collective motion of nanoparticles: the directed motion with certain velocity, rotary motion, and alternation of the stated motion modes.

In contrast to the work [17], we are interested in the case of hard self-organization mode when velocity

---

* yushchenko@phe.sumdu.edu.ua

of nanoparticles motion is changed not smoothly, but stepwise. To this end, we take into account the simplest approximation [20] for the time of change of the order parameter which depends on the velocity value v.

As a result, expression for the average acceleration is written in the form

$$\dot{v} = -\frac{v}{t_v}\left(1 + \frac{\eta}{1 + v^2/v_\eta^2}\right) + a_v h .\qquad(1)$$

Here t_v is the typical time of change of the average velocity of nanoparticles; η is the dispersion constant of the average velocity relaxation time; v_η is the dispersion scale; $a_v > 0$ is the positive constant of linear reaction of acceleration $\dot{v}$ on the increase in the field h.

Equation for the conjugate field is taken in standard form

$$\dot{h} = -\frac{h}{t_h} + a_h v \varepsilon ,\qquad(2)$$

where the first term has relaxation nature with typical time t_h; the second one represents positive feedback of the average velocity of motion and internal energy with the rate of the field ($a_h > 0$ is the positive coupling constant). Exactly the latter conditions the increase in the field which is the reason of self-organization.

The evolution equation of the internal energy

$$\dot{\varepsilon} = \frac{(\varepsilon_e - \varepsilon)}{t_\varepsilon} - a_\varepsilon v h + \zeta(t)\qquad(3)$$

differs from equations (1)-(2) by the fact that relaxation of the parameter ε occurs not to zero but to finite value ε_e which is specified by the external conditions, for example, by the temperature of liquid in which suspended nanoparticles are placed (t_ε is the corresponding relaxation time, constant $a_\varepsilon > 0$). Also, in accordance with the Le Chatelier principle, the negative feedback of the external field and velocity of nanoparticles motion with the rate of the internal energy is taken into account in equation (3). Moreover, considering the random influence of environment, stochastic source representing the Ornstein-Uhlenbeck process is added to equation (3)

$$\langle \zeta(t) \rangle = 0, \ \langle \zeta(t), \zeta(t') \rangle = \frac{I}{\tau}\exp\left(-\frac{|t - t'|}{\tau}\right).\qquad(4)$$

Here I specifies the intensity of fluctuations and τ – the time of their relaxation.

According to [20], system of synergetic equations (1)-(3) represents the simplest field scheme describing the self-organization effect. For the analysis of this system, it is convenient to use dimensionless variables, namely, the reduced time t, average velocity v, field h, internal energy ε, and intensity of fluctuations I to the corresponding scales

$$t_v, \ \left(a_h a_\varepsilon t_h t_\varepsilon\right)^{-1/2}, \left(a_v^2 t_v^2 a_h a_\varepsilon t_h t_\varepsilon\right)^{-1/2}, \left(a_h t_h a_v t_v\right)^{-1}, \left(t_\varepsilon a_h t_h a_v t_v\right)^{-2}.$$

As a result, the behavior of a group of active nanoparticles is represented by the dimensionless system of equations

$$\dot{v} = -v\left(1 + \frac{\eta}{1 + v^2/v_\eta^2}\right) + h ,\qquad(5)$$

$$\sigma^{-1}\dot{h} = -h + v\varepsilon ,\qquad(6)$$

$$\delta^{-1}\dot{\varepsilon} = (\varepsilon_e - \varepsilon) - vh + \zeta(t),\qquad(7)$$

where correlations $\sigma^{-1} \equiv t_h/t_v, \delta^{-1} \equiv t_\varepsilon/t_v.$ are introduced.

In a general case, system (5)-(6) does not have analytical solution, and therefore, we will use the following approximation:

$$t_h \simeq t_v \gg t_\varepsilon ,\qquad(8)$$

which shows that internal energy of particles is changed fastest during system evolution. In this case, $\sigma = 1$ and $\delta \gg 1$. The last condition allows to neglect the left side of equation (7). As a result, system of three differential equations is reduced to two ones

$$\dot{v} = -v\left(1 + \frac{\eta}{1 + v^2/v_\eta^2}\right) + h ,\qquad(9)$$

$$\dot{h} = -\sigma h + \sigma v\left[\varepsilon_e - vh + \xi(t)\right].\qquad(10)$$

Substituting expressions for h and $\dot{h}$ obtained from (9) into equation (10), we come to one second-order differential equation

$$\ddot{v} + \gamma(v)\dot{v} = f(v) + g(v)\zeta(t),\qquad(11)$$

which has canonical form of the equation of motion for non-linear stochastic Van der Pole oscillator [17, 20-23]. In our case, friction coefficient $\gamma(v)$, force $f(v)$, and noise amplitude $g(v)$ are determined by expressions

$$\gamma(v) = 1 + \eta\left(\frac{1 - v^2/v_\eta^2}{\left(1 + v^2/v_\eta^2\right)^2}\right) + \sigma\left(1 + v^2\right),$$

$$f(v) = \sigma(\varepsilon_e - 1)v - \sigma v^3 - \sigma\eta\frac{v\left(1 + v^2\right)}{1 + v^2/v_\eta^2},\qquad(12)$$

$$g(v) = \sigma v.$$

3. STATISTICAL ANALYSIS OF SYNERGETIC DISTRIBUTION

Now the problem is to find the distribution function $P(v, a, t)$ of the system in phase space generated by the velocity v and acceleration a [17, 21, 24].

To this end, we will present the Euler equation (11) within the framework of the Hamilton formalism

$$\dot{v} = a,$$
$$\dot{a} = -\gamma(v)a + f(v) + g(v)\zeta(t).\qquad(13)$$

As a result, necessary probability density $P(v, a, t)$ is reduced to the distribution function $\rho(v, a, t)$ of the solutions of system (13)

$$P(v, a, t) = \langle \rho(v, a, t) \rangle_\zeta .\qquad(14)$$

Here $\langle ... \rangle_\zeta$ corresponds to the averaging over noise ζ.

The continuity equation is written in standard form [20, 24]

$$\left[\frac{\partial}{\partial t} + \hat{L}(v,a) \right] \rho(v,a,t) = -g(v)\zeta(t)\frac{\partial}{\partial a}\rho(v,a,t), \quad (15)$$

where operator

$$\hat{L}(v,a) = -\gamma(v)\frac{\partial}{\partial a}a + a\frac{\partial}{\partial v} + f(v)\frac{\partial}{\partial a} \qquad (16)$$

is introduced. In accordance with expansion method over van Kampen cumulants [24, 25], expression for the averaged function $\rho(v, a, t)$ takes the form of integral-differential equation

$$\left[\frac{\partial}{\partial t} + \hat{L}(v,a) \right]\langle \rho(v,a,t) \rangle = -\frac{\partial}{\partial a}g(v)\times$$

$$\times \int_0^t \langle \zeta(t)\zeta(t') \rangle e^{-\bar{L}(t-t')}g(v)\frac{\partial}{\partial a}\langle \rho(v,a,t) \rangle dt'. \quad (17)$$

Then we proceed to the initial distribution $P(v, a, t)$ replacing operator in the left side of equation (17) by $\hat{N}$

$$\left\{ \frac{\partial}{\partial t} + \hat{L}(v,a) \right\} p(v,a,t) = \hat{N}(v,a,t)p(v,a,t). \quad (18)$$

Since we consider the system on large time scales, then according to [24] equation (11) can be represented in the form

$$\ddot{v}_i + \gamma(v_i)\dot{v}_i = f(v_i) + g(v_i)\zeta_i(t) \qquad (19)$$

for set of variables $v_1, v_2, ..., v_n$ and $\zeta_1, \zeta_2, ..., \zeta_n$, where summation over repetitive indexes is meant. Analyzing expression (19), instead of integral-differential operator $\hat{N}$ we obtain the sum

$$\hat{N}(v,a,t) = \sum_{n=0}^{\infty} \hat{N}_n = g(v)\frac{\partial}{\partial a}\sum_{n=0}^{\infty} M_n \hat{L}_n(v,a), \quad (20)$$

where moments of correlation function are determined as follows

$$M_n(t) = \frac{1}{n!}\int_0^\infty t^n \langle \zeta(t)\zeta(0) \rangle dt. \qquad (21)$$

Using representation (4), we obtain correlation for zero and first moments

$$M_0(t) = I, \quad M_1(t) = I\tau. \qquad (22)$$

Operators $\hat{L}_n$ are defined by the rule [17, 21, 24]

$$\hat{L}_n = \left[\hat{L}_{n-1}, \hat{L} \right], \quad \hat{L}_0 = g(v)\frac{\partial}{\partial a}, \qquad (23)$$

where square brackets denote the commutator $[A, B] = = AB - BA$.

Expressions for $\hat{N}_0$ and $\hat{N}_1$ allow to represent expression (18) in the form of the Kramers equation [26], whose solution is the function $P(v, a, t)$.

Since integral

$$p(v,t) = \int_a P(v,a,t)da \qquad (24)$$

is of a greater practical interest than function $P(v, a, t)$ does, then later we consider the moments of the initial distribution

$$p_n(v,t) = \int_a a^n P(v,a,t)da. \qquad (25)$$

In this case, zero moment $p_0(v,t) \equiv p(v,t)$ will be the required one [20, 24].

After multiplication by a^n of the Kramers equation and acceleration integration, we obtain the recurrent correlations [20, 24] which result in the closed hierarchical system of equations for the moments of the distribution function

$$\frac{\partial p}{\partial t} = -\frac{\partial p_1}{\partial v},$$

$$\gamma p_1 = f p - \frac{\partial p_2}{\partial v} - M_1\left[g\frac{\partial g}{\partial v}p + g^2\frac{\partial p}{\partial v} \right], \qquad (26)$$

$$\gamma p_2 = g^2\left(M_0 - M_1\gamma \right)p.$$

For brevity, dependence on the velocity v will be omitted here and further.

Solving cyclic system of equations (26), we come to the Fokker-Plank equation [27]

$$\frac{\partial p}{\partial t} = -\frac{\partial}{\partial v}\left(D_1 p \right) + \frac{\partial^2}{\partial v^2}\left(D_2 p \right), \qquad (27)$$

where

$$D_1 = \frac{1}{\gamma}\left[f - M_0\frac{g^2}{\gamma^2}\frac{\partial\gamma}{\partial v} + M_1 g\frac{\partial g}{\partial v} \right], \qquad (28)$$

$$D_2 = M_0\frac{g^2}{\gamma^2} \qquad (29)$$

are the drift and diffusion coefficients, respectively.

4. LANGEVIN EQUATION

Langevin equation, which describes evolution of the order parameter,

$$\dot{v} = D_1 + \sqrt{2D_2}\xi(t) \qquad (30)$$

is assigned to the Fokker-Plank equation (27) [20, 27]. Here $\xi(t)$ is the white noise with standard properties

$$\langle \xi(t) \rangle = 0, \quad \langle \xi(t), \xi(t') \rangle = \delta(t - t'). \qquad (31)$$

When studying transitions between modes of nanoparticles motion, we will use usual approach [28]. To this end, we write the Langevin equation (30) in the form of stochastic differential equation

$$dv = D_1 dt + \sqrt{2D_2}dw, \qquad (32)$$

where $dw = \xi(t)dt$ represents the Wiener process [27]. This allows to introduce a new process $z(t)$ with transition Jacobian $dz/dv = \left(\sqrt{2D_2} \right)^{-1}$.

Since initially a white noise was used, then for the variable $z(t)$ a stochastic operator of differentiation can be written in the form of [21]

$$dz = \frac{dz}{dv}dz + \frac{1}{2}\frac{d^2z}{dz^2}(dz)^2. \qquad (33)$$

Having obtained by such a way the evolution equation for the process $z(t)$, we come to the expression for white noise

$$\xi(t) = \frac{\dot{v} - D_1 + \frac{1}{2}D_2'}{\sqrt{2D_2}}, \qquad (34)$$

where prime denotes velocity v differentiation. Taking into account expression for the probability density $p(\xi(t)) \propto \exp(-1/2 \int \xi^2(t)) dt$ and correlation $p(v) = p(\xi)J$ between distributions (J is the Jacobian of the transition from variable ξ to variable v), according to [29] we obtain the following expression:

$$p(v,\dot{v},t) \propto \exp\left(-\frac{1}{2}Ldt\right), \qquad (35)$$

where L plays the role of Lagrangian in the Euclidean field theory

$$L = \frac{1}{2D_2}\left(\dot{v} - D_1 + \frac{1}{2}D_2'\right)^2. \qquad (36)$$

In the stationary state, acceleration of particles $\dot{v} = 0$ and extremum condition $\partial L/\partial v = 0$ for Lagrange function leads to the system of equations

$$
\begin{aligned}
D_1 - D_2' &= 0, \\
2D_2(D_2'' - D) - (D_2')^2 + D_1 D_2' &= 0.
\end{aligned} \qquad (37)
$$

Substituting into (37) dependences (12), (22), (28), and (29) we obtain phase diagram of the system (Fig. 1a) and dependence of the stationary value of average velocity of nanoparticles motion on the value of internal energy specified by external conditions (Fig. 1b).

As seen from Fig. 1a, presence of four regions *A*, *B*, *C*, and *D* on the phase diagram is typical for the studied system. In order to characterize the modes of motion inherent to each region, we consider in detail Fig. 1b, where solid thick line denotes the solution of the first equation of (37); rays *A*, *B*, *C*, and *D* answer the corresponding points of the phase diagram; straight lines 1 and 2 represent additional solutions arising during the analysis of the second equation of (37). In this case, points *R* corresponding to $v = 0$ characterize rotational motion of particles; average velocity for points *M* and *T* $v \neq 0$, therefore, the directional rectilinear motion takes place; points *N* do not have physical meaning and correspond to additional extremums separating stationary states of the system; points *K* and *L* are also additional solutions obtained from the second equation of (37).

Besides the analysis of stationary states of the system, later we should consider kinetics of the transition from one state to another.
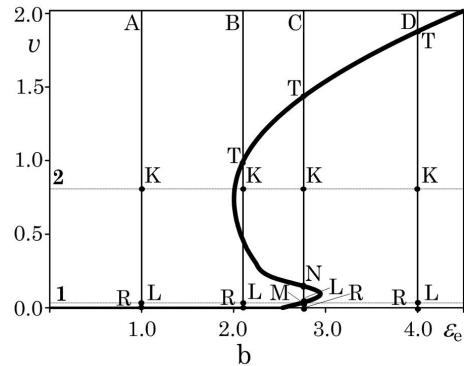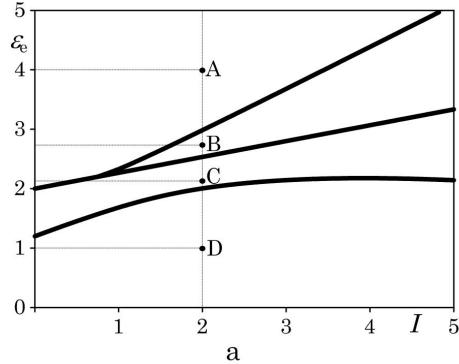

Fig. 1 – State diagram of the system (a) and dependence of the stationary value of the average velocity of motion (b) at $I = 2$, $\tau = 0,4$, $v_\eta = 0,1$.

5. PHASE PORTRAITS OF THE SYSTEM

For the analysis of system kinetics we consider the Euler-Lagrange equation

$$\frac{\partial L}{\partial v} - \frac{d}{dt}\frac{\partial L}{\partial \dot{v}} = \frac{\partial R}{\partial \dot{v}}. \qquad (38)$$

Since in the studied system it is necessary to take into consideration energy dissipation, then in equation (37) we have took into account the dissipative function whose standard form is $R = \dot{v}^2/2$. As a result, we come to the second-order differential equation

$$\ddot{v} + \dot{v}D_2 - \frac{D_2'}{2D_2}\left[\dot{v}^2 - (D_2 - D_2')^2\right] + (D_1 - D_2')\cdot(D_2'' - D_1') = 0, \quad (39)$$

which can be represented as the system of two first-order differential equations. The given transformation allows to use the phase plane method for the consideration of the system kinetics based on the phase portraits on the plane $(\dot{v}, v)$.

Phase portraits of the system are shown in Fig. 2 and answer the corresponding regions of the phase diagram (primes denote the points which correspond to the inverse direction of the velocity v).

Analyzing the phase portraits, one can conclude about rather complex kinetics of the studied stochastic system. In this case, directional motion of suspended nanoparticles is possible with different average velocities $v \neq 0$ (saddles *M* and *T* in Fig. 2b, c, d); non-standard kinetic behavior is typical for the rotational motion (a special point *R* in Fig. 2a-d).
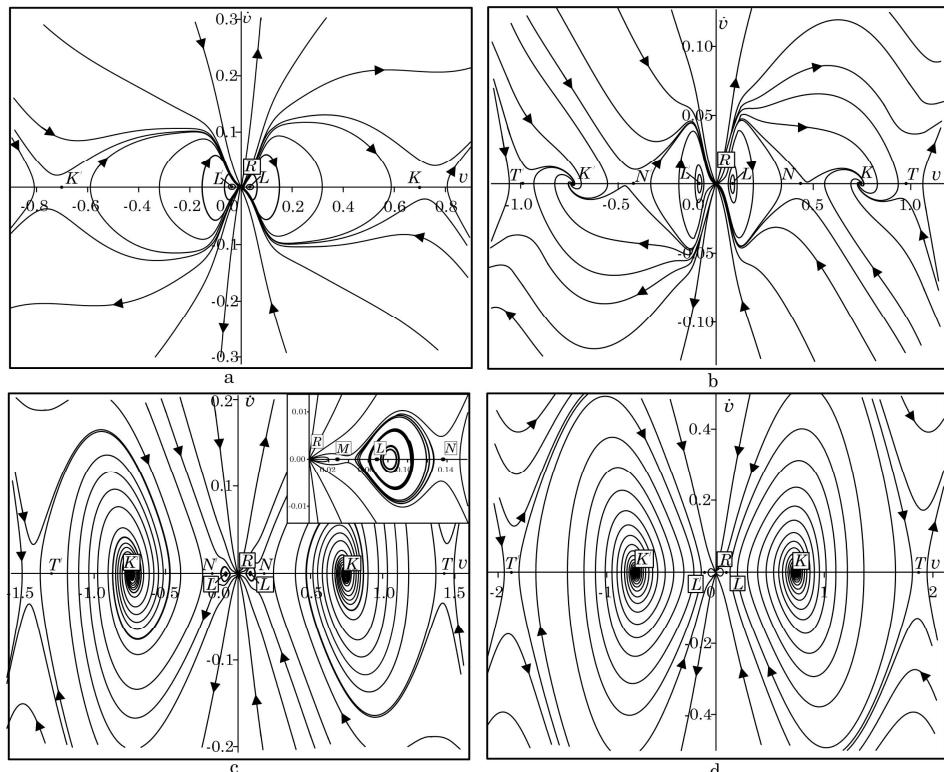
Fig. 2 – Phase portraits of the system for the parameters denoted by the points *A, B, C* and *D* on the phase diagram (Fig. 1a)

Moreover, one can say that only rotational motion is realized for region *A* of the phase diagram; coexistence of the rotational and directional motion types is typical for region *B*; two types of the directional motion with different values of the velocity *v* are possible in the third region *C*; and only directional motion of nanoparticles is realized in the last region *D* of the phase diagram.

6. CONCLUSIONS

The self-consistent model which allows to describe the possible motion types of suspended nanoparticles is constructed as a result of the performed investigation. Considering the effect of environment which influences the value of the internal energy ε_e specified by the temperature of surrounded liquid, possible combinations of existing motion modes were studied. In this case, only rotational motion of nanoparticles is possible for small values of the internal energy ε_e and wide range of the intensities *I*. Otherwise, in the case of small intensity of fluctuations and large value of the internal energy ε_e, a single directional motion with sufficient average velocity takes place. In the intermediate cases, two modes of coexistence are possible: rotational and directional motion; directional motion with different velocities (one of which takes highly insignificant values).

The given results can be useful for both in solving some physical problems, for example, control of nanoparticles motion in catalytic reactors, and in medical problems where drug delivery to the specified place of an organism is rather promising nowadays.

REFERENCES

1. M. Bazant, O. Vinogradova, *Phys. Rev. Lett.* **102**, 026001 (2009).
2. C. Moreau, J. Dupuis, J. Revilloud, K. Arumugam, M. Vivaudou, *Nat. Nanotechnol.* **3**, 620 (2008).
3. U. Demirok, R. Laocharoensuk, K. Manesh, J. Wang, *Angew. Chem.* **120**, 9489 (2008).
4. J. Gibbs, Y. Zhao, *Phys. Let.* **94**, 163104 (2009).
5. N. Kovtyukhova, *J. Phys. Chem. C* **112**, 6049 (2008).
6. R. Laocharoensuk, J. Burdick, J. Wang, *ACS Nano* **2**, 1069 (2008).
7. W. Paxton, K. Kistler, C. Olmeda, A. Sen, S. Angelo, Y. Cao, T. Mallouk, P. Lammert, V. Crespi, *J. Am. Chem. Soc.* **126**, 13424 (2004).
8. Y. Wang, R. Hernandez, D. Bartlett, J. Bingham, T. Kline, A. Sen, T. Mallouk, *Langmuir* **22**, 10451 (2006).
9. P. Ramachandran, R. Chaudhari, *Three phase cata-lytic reactors* (London: Gordon and Breach: 1983).
10. J. Enterkin, K. Poeppelmeier, L. Marks, *Nano Lett.* **11**, 993 (2011).
11. D. Rings, R. Schachoff, M. Selmke, F. Cichos, K. Kroy, *Phys. Rev. Lett.* **105**, 090604 (2010).
12. P. Radtke, L. Schimansky-Geier, *Phys. Rev. E* **85**, 051110 (2012).
13. L. Joly, S. Merabia, J.-L. Barrat, *EPL* **94**, 50007 (2011).
14. R. Golestanian, *Phys. Rev. Lett.* **102**, 188305 (2009).
15. Y. Hong, N. Blackman, N. Kopp, A. Sen, D. Velegol, *Phys. Rev. Lett.* **99**, 178103 (2007).
16. J. Howse, R. Jones, A. Ryan, T. Gough, R. Vafabakhsh, R. Golestanian, *Phys. Rev. Lett.* **99**, 048102 (2007).
17. O. Yushchenko, A. Badalyan, *Phys. Rev. E* **85**, 051127 (2012).
18. G. Ivanitskii, A. Medvinskii, M. Tsyganov, *Phys. Usp.* **37**, 961 (1994).

19. G. Ivanitskii, A. Medvinskii, M. Tsyganov, *Phys. Usp.* **34**, 289 (1991).
20. A. Olemskoi, *Sinergetika slozhnyh sistem. Fenomenologiya i statisticheskaya teoriya* (M.: KRASAND: 2009).
21. A. Khomenko, D. Kharchenko, O. Yushchenko, *Visnyk L'vivs'kogo derzhavnogo universytetu* **37**, 44 (2004).
22. C. Gardiner, *Handbook of Stochastic Methods: for Physics, Chemistry and the Natural Sciences* (Berlin: Springer: 2004).
23. A. Balanov, N. Janson, D. Postnov, O. Sosnovtseva, *Synchronization. From Simple to Complex* (Verlag Berlin Heidelberg: Springer: 2009).
24. V. Shapiro, *Phys. Rev. E* **48**, 109 (1993).
25. N. Kampen, *Stochastic Processes in Physics and Chemistry* (Amsterdam: Elsevier: 2007).
26. H. Kramers, *Phisica* **7**, 284 (1940).
27. H. Risken, *The Fokker-Planck education* (Berlin: Springer: 1989).
28. Z. Zinn-Justin, *Quantum Field Theory and Critical Phenomena* (Oxford: Clarendon Press: 1994).
29. G. Roepke, *Neravnovesnaya statisticheskaya mekhanika* (M.: Mir: 1990).