

MODELING OF MASS-EXCHANGE PROCESSES TAKING INTO ACCOUNT
FLUCTUATIONS OF THE PHYSICO-CHEMICAL PARAMETERS

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The Kolomogorov-Fokker-Planck equation is used to describe the kinetics of mass exchange, taking into account fluctuations of the main physical and chemical parameters. In a particular case, we present a solution of the problem.

In the description of the kinetics of an arbitrary process, one considers the change of some quantities which characterize a real process in time and space. In mass-exchange processes, the calculation is usually carried out using average physical parameters (concentration of a component, temperature, velocity of motion of the materials, etc.). However, in many situations, for example, in desiccation, adsorption (desorption), extraction, grinding or mixing, the description of the processes in terms of the average quantities does not give exhausting information, and does not satisfy the requirements which are imposed by the technological practice. Usually, all technological processes which involve processing of dispersed media are by their nature random, and contain fluctuations of the main physical parameters. In mass-exchange processes, the random changes of these parameters can be caused by the polydisperse nature of the materials, collisions of the dispersed media, pulsating velocity field (in particular, turbulent pulsations), circulation current, containment conditions, fluctuations of the external conditions, etc. In many real processes in real systems, it is therefore necessary to take into account the stochastic nature of these processes and to estimate the distribution of the degree of processing (uniformity) of the materials.

Romankov et al. [1] made an attempt in this direction but did not take into account the physical foundations of the process. The solution of the problem by classical methods, using averaging of the turbulent motion and averaging in the mechanics of dispersed media, is difficult. In the present work we present a simplified method which uses the theory of Markov diffusion processes.

The processes under consideration can be characterized by a multidimensional probability density function $w(\bar{\xi}, t)$ of points which describe the corresponding phenomenon in the phase space, where $\bar{\xi}(t) = \{\xi_1(t), \xi_2(t), \dots, \xi_n(t)\}$. The method of [2] will be used to derive an equation satisfied by $w(\bar{\xi}, t)$. Let us suppose that $\bar{\xi}(t)$ satisfies a system of kinetic equations

$$\frac{d\bar{\xi}_i(t)}{dt} = F_i(\bar{\xi}, t) + F'_i(\bar{\xi}, t), \quad \bar{\xi}(0) = \bar{\xi}_0, \quad (1)$$

where $F_1(\bar{\xi}, t)$ is a deterministic function, and $F'_1(\bar{\xi}, t)$ is a Gaussian random field delta-correlated in time, with average value $\langle F'_i(\bar{\xi}, t) \rangle = 0$. The random process $\bar{\xi}(t)$ is then a Markov diffusion process, and $w(\bar{\xi}, t)$ satisfies the Kolmogorov-Fokker-Planck equation [2-4]:

$$\frac{\partial w(\bar{\xi}, t)}{\partial t} = - \sum_{i=1}^n \frac{\partial}{\partial \bar{\xi}_i} [k_i(\bar{\xi}, t) w(\bar{\xi}, t)] + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n \frac{\partial^2}{\partial \bar{\xi}_i \partial \bar{\xi}_j} [k_{ij}(\bar{\xi}, t) w(\bar{\xi}, t)], \quad (2)$$

where the first and second infinitesimal moments (drift and diffusion coefficients) of variation of the random quantity $\bar{\xi}(t)$ $k_i(\bar{\xi}, t)$ and $k_{ij}(\bar{\xi}, t)$ are calculated from (1) using known rules [2, 4]. In other words, the nonlinear dynamical system (1) is replaced by the extensively studied equation (2) for the probability density which completely describes the process. We should note here that if the drift coefficients are linear functions of $\xi_i(t)$,

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$$k_i(\bar{\xi}, t) = \sum_{j=1}^n a_{ij} \xi_j(t) + a_i.$$

and the diffusion coefficients are constant, $k_{ij}(\bar{\xi}, t) = \text{const}$, the multidimensional process $\bar{\xi}(t)$ is Gaussian, and it is possible in this case to obtain a general solution of Eq. (2) [4]. Equation (2) is obtained under the assumption that the random field $F_1'(\bar{\xi}, t)$ is delta-correlated in time. In real conditions, the random fields $F_1'(\bar{\xi}, t)$ have finite correlation radius τ_0 in time, and this approximation is a good one only if the time τ_0 is much smaller than the characteristic times of change of the dynamical system (1). In the general case of non-delta-correlated processes, one can construct a method of successive approximations in which the present approximation is the first step. The subsequent approximations take into account the finiteness of the time correlation radius τ_0 and lead to a system of closed operator equations [2]. For dynamical systems with non-Gaussian fluctuations of parameters, one can also obtain an approximation in terms of a Markov process. For example, for Poisson fluctuations, one obtains the Kolmogorov-Feller integro-differential equation [2], rather than Eq. (2).

If the system is described by stochastic equations

$$\frac{d\xi_i(t)}{dt} = F_i[\bar{\xi}, \bar{F}'(\bar{\xi}, t)], \quad \xi_i(0) = \xi_{i0}, \quad (1')$$

where $F_i(\bar{\xi}, \bar{F})$ are deterministic functions, and $F'(\bar{\xi}, t) = \{F_1'(\bar{\xi}, t), F_2'(\bar{\xi}, t), \dots, F_n'(\bar{\xi}, t)\}$ are Gaussian random fields, it is in general impossible to obtain a closed equation for the probability density $w(\bar{\xi}, t)$. However, for sufficiently small fluctuations $\bar{F}'(\bar{\xi}, t)$, the right-hand side in Eq. (1') can be expanded in a series in powers of the function $\bar{F}'(\bar{\xi}, t)$ and obtain the corresponding equation (2) in the linear approximation. It should be noted that the above discussion of the system (1) carries over without change to the case of a system of integrodifferential equations of the form

$$\frac{d\xi_i(t)}{dt} = F_i(\bar{\xi}, t) + \int D_{ij}(\bar{\xi}, \bar{y}, t) F_j'(\bar{y}, t) d\bar{y}, \quad \xi_i(0) = \xi_{i0}, \quad (1'')$$

where $D_{ij}(\bar{\xi}, \bar{y}, t)$ is a deterministic tensor function, and if $D_{ij}(\bar{\xi}, \bar{y}, t) = \delta_{ij} \delta(\bar{\xi} - \bar{y})$, Eq. (1'') reduces to (1) [2]. Noting the above considerations we shall below, without a loss of generality, consider only a dynamical equation of the form (1). It is necessary that each component $\xi_i(t)$ is a Markov process so that the complete process $\bar{\xi}(t)$ is a Markov diffusion process [4].

For mass-exchange processes, the probability density $w(\bar{\xi}, t)$ will be represented in the form $w(\bar{\xi}, t) = w(\bar{\xi}, r, t)$, where $w(\bar{\xi}, r, t) dr d\bar{\xi}$ is a fraction (number) of particles of the material which lie in the volume $(r, r + dr)$ with their properties in the interval $(\bar{\xi}, \bar{\xi} + d\bar{\xi})$, at time t . The coordinates ξ_i can be the concentration of the corresponding phase components, temperature, etc.

We consider a sufficiently representative ensemble of dispersed materials which take part in the mass transfer and assume that it is characterized by a continuous distribution of concentrations of the corresponding components over the particles (volume). The kinetic equation (1) can then be written in the form

$$\frac{dc_i}{dt} = F_i(\bar{X}, t) + F_i'(\bar{X}, t), \quad \frac{dr}{dt} = \bar{V} + \bar{V}', \quad i = \overline{1, n}. \quad (3)$$

Here we assume that the process has no "memory" and the temperature fluctuations will not be determined, although it can be done. It should be noted here that the assumption of Markov nature of the mass-exchange process is not always exactly satisfied, and the corresponding Kolmogorov-Fokker-Planck equation is the first approximation of the real process which can, in many cases, be assumed justified with respect to the system (1) in view of the above considerations. The nonlinear equations (3) can be ascribed corresponding Kolmogorov-Fokker-Planck equations. Here, if one cannot neglect the inertial of the particles, the velocity field must be included among the coordinates ξ_i in the phase space, and the system (3) must be supplemented by the momentum conservation laws of the corresponding phases, taking into account fluctuations. For a two-phase medium, these equations (which include the fluctuating terms) were obtained in [5] by the methods of ensemble averages.

In the present method for the description of processes in heterogenous systems by using the random diffusion quantities, the main point is the construction of the kinetic equations (1). To this end, it is necessary to solve hydrodynamic or other appropriate problems by using all the available a priori information. In the mass-exchange processes, this reduces to the simultaneous solution of the hydrodynamic equations, and the equation for the internal or external convective diffusion. In other words, the function $F_i(\bar{X}, t)$ can be constructed by using the solution of the equations for multivelocitity continua and an averaging method in the mechanics of heterogeneous media [5, 6]. One should note here that the determination of the concentration fluctuations and, consequently, the distribution over the degree of processing can be attempted by using a direct solution of the mass-balance equation and the equations of thermohydrodynamics [7], taking into account the fluctuations of the main physical parameters. However, to solve these equations simultaneously even for the simplest realistic systems is very difficult. Therefore, the above method makes it possible to overcome some of these difficulties. For example, one first solves an idealized and, in some sense, a model problem. Using this, one constructs the functions $F_i(\bar{X}, t)$ and, subsequently, one takes into account the fluctuations and nonideality.

For example, in conditions of complete absorption of matter on the surface of particles, one can write down the relation

$$v_k \frac{dc_{ki}}{dt} = I_i = \iint_{s_k} \left(D_{ef} \frac{\partial c_i}{\partial n} \right)_{s_k} ds_k. \quad (4)$$

The right-hand side of (4) can be determined using numerous known theoretical and experimental studies, for example, according to [8]. In other words, the functions $F_i(\bar{X}, t)$ can be determined in the simplest cases. Or, having in mind simple homogeneous media, one can introduce a nonlinear approximation of the general expression for the currents I_i in the form of a series

$$F_i(\bar{X}, t) \sim I_i = \sum_{j, (i)=1}^n L_{ij} X_j + \frac{1}{2!} \sum_{j, (i), k=1}^n L_{ijk} X_j X_k + \dots + \frac{1}{q!} \sum_{j, (i), k, q=1}^n L_{i,j,k,\dots,q} X_j, X_k, \dots, X_q. \quad (5)$$

Further, by extending the method to engineering approximations for quasilinear and linear solutions one can easily obtain a result which is equivalent to a principle of linear thermodynamics of reversible processes, the Onsager approximation. According to [7], the driving force X_j can be represented in the form of an additive function

$$X_j = \left(\frac{\mu_{ni}}{T_n} - \frac{\mu_{ki}}{T_k} \right) + i_{i(nk)} \left(-\frac{1}{T_k} - \frac{1}{T_n} \right) + \left(\frac{\bar{V}_{nk} - \bar{V}_k}{2T_k} \right)^2 - \left(\frac{\bar{V}_{nk} - \bar{V}_n}{2T_n} \right)^2, \quad (6)$$

which determines the rate of transport of component i between phases n and k .

For simplicity, we consider below two-phase systems in which the mass exchange of some key component c takes place, principally because of the driving force $X = \left(\frac{\mu_{1i}}{T_1} - \frac{\mu_{2i}}{T_2} \right)$.

To solve this problem, the chemical potentials must be expressed in terms of the concentration of the key component and in terms of other physical parameters (temperature and pressure) whose general functional dependence for realistic systems is unknown. Thus, in the first approximation, the function $F(\bar{X}, t)$ can be represented in the form

$$F(\bar{X}, t) \approx K(c_p - c), \quad (7)$$

where K is a complicated function of hydrodynamic conditions and the state of the system which can be determined from the simultaneous solution of the hydrodynamic problem and the convective diffusion equations or experimentally. Using (3) and (7), Eq. (2) then takes the form

$$\begin{aligned} \frac{\partial w(c, \bar{r}, t)}{\partial t} = & - \sum_{j=1}^3 \frac{\partial}{\partial X_j} [V_j(c, \bar{r}, t) w(c, \bar{r}, t)] + \\ & + \frac{\partial}{\partial c} [K(c - c_p) w(c, \bar{r}, t)] + \frac{1}{2} \sum_{i=1}^4 \sum_{j=1}^4 \frac{\partial^2}{\partial X_i \partial X_j} [\sigma_{ij} w(c, \bar{r}, t)], \end{aligned} \quad (8)$$

where V_j are the components of the average velocity of motion of the dispersed phase, σ_{ij} are the diffusion coefficients $K_{ij}(\bar{x}, t)$, and $X_4 = c$.

Equation (8) describes the distribution of particles along trajectories in the phase space, and its solution describes completely the mass-exchange process. For the solution of Eq. (8), one must specify the initial distribution $x(c, \bar{r}, 0)$ and appropriate boundary conditions which should be formulated by taking into account a specific real process. Equation (8) should be considered together with the hydrodynamic problem. In general, V_j and σ_{ij} are functions of state of the system, coordinates and time, and the problem can be solved only by approximate methods. If one considers the particular case of a system with concentrated parameters when the mass exchange of one key component c takes place, (8) can be written in the form

$$\frac{\partial w(c, t)}{\partial t} = \frac{\partial}{\partial c} [K(c, t)(c - c_p)w(c, t)] + \frac{1}{2} \frac{\partial^2}{\partial c^2} [\sigma w(c, t)], \quad (9)$$

which will be solved for the initial distribution

$$w(c, 0) = f(c) \quad (10)$$

and boundary conditions

$$G[w(c_{\min}, t)] = 0, \quad G[w(c_{\max}, t)] = 0, \quad (11)$$

$$G[w(c, t)] = K(c, t)(c - c_p)w(c, t) + \frac{1}{2} \frac{\partial}{\partial c} [\sigma w(c, t)],$$

which indicate that there is no flow across the boundary of the representative points, where σ is the intensity of random pulsations ("white noise"). Depending on the realization of the mass-exchange process and on the type of the apparatus, other forms of boundary conditions are also possible.

From Eq. (9), one can obtain the known equation for the mass exchange with average concentration $\bar{c} = \int_{c_{\min}}^{c_{\max}} cw(c, t)dc$ in the form

$$\frac{d\bar{c}}{dt} = -K(\bar{c} - c_p). \quad (12)$$

To obtain the solution of the problem (9)-(11), we use the method of finite integral transform [10] which, in the present case, has the form

$$\bar{w}(\gamma, t) = \int_{c_{\max} - c_p}^{c_{\min} - c_p} w(z, t) P(z) M(z, \gamma) dz, \quad (13)$$

where $M(z, \gamma)$ is the kernel of the integral transform, $P(z)$ is a weight function which brings the differential operator on the right-hand side of Eq. (9) to the self-adjoint form, and $z = c - c_p$. The solution of the problem (9)-(11) for $K(c, t) \approx \text{const}$ can be written in the form

$$w(z, t) = \sum_{n=1}^{\infty} w_n(0) \exp[-K(\lambda_n - 1)t] M_n(z), \quad (14)$$

where $M_n(z)$ are the eigenfunctions which correspond to the eigenvalues λ_n of the Weber differential equation [11], and $w_n(0)$ is determined from the initial condition (10). Figure 1 shows the results of calculations using formula (14) for various values of the parameters. The degree (uniformity) of processing (mass exchange) depends strongly on the ratio k/σ and on the value of σ . The dispersion increases with increasing ratio k/σ . For example, the average concentration $m(c)$ and dispersion $D(c)$ for various values of k/σ for the steady-state distribution are as follows: 1) $k/\sigma = 10$; $m(c) = 0.1298$; $D(c) = 0.6772 \cdot 10^{-2}$; 2) $k/\sigma = 100$; $m(c) = 0.544 \cdot 10^{-1}$; $D(c) = 0.1815 \cdot 10^{-2}$; 3) $k/\sigma = 310$; $m(c) = 0.327 \cdot 10^{-1}$; $D(c) = 0.58 \cdot 10^{-3}$; 4) $k/\sigma = 1510$; $m(c) = 0.16 \cdot 10^{-1}$; $D(c) = 0.12 \cdot 10^{-3}$; 5) $k/\sigma = 3310$; $m(c) = 0.10 \cdot 10^{-1}$; $D(c) = 0.53 \cdot 10^{-4}$; 6) $k/\sigma = 8110$, $m(c) = 0.69 \cdot 10^{-2}$; $D(c) = 0.21 \cdot 10^{-4}$. The results of the calculations show that it is important to take into account random factors, since for large values of dispersion which correspond to small values of k/σ , the description of the mass-exchange process in terms of the average concentration does not give complete information about the process.

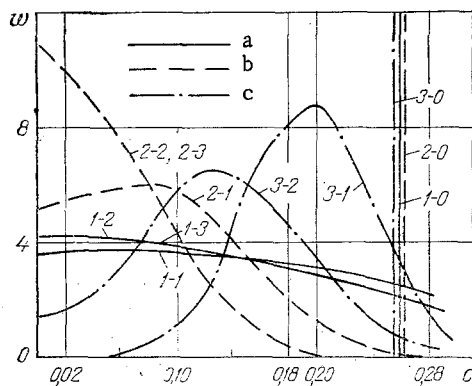


Fig. 1. Probability density $w(c, t)$ for the initial distribution $f(c) = \delta(c - c_0)$ at various times ($c_p = c_{\min} = 0.001$; $c_{\max} = 0.3$; $c_0 = 0.25$; $K_1 = K/3600$): a) $K/\sigma = 10$, $K_1 = 10 \text{ sec}^{-1}$. 1-0: $t = 0 \text{ sec}$; 1-1: $t = 154.8 \text{ sec}$; 1-2: $t = 864 \text{ sec}$; 1-3: stationary distribution. b) $K/\sigma = 100$ $K_1 = 10 \text{ sec}^{-1}$: 2-0: $t = 0 \text{ sec}$; 2-1: $t = 360 \text{ sec}$; 2-2: $t = 2160 \text{ sec}$; 2-3: stationary distribution. c) $K/\sigma = 100$, $K_1 = 1 \text{ sec}^{-1}$: 3-0: $t = 0 \text{ sec}$; 3-1: $t = 864 \text{ sec}$; 3-2: $t = 2404.8 \text{ sec}$.

When the parameters σ , k , c_p , c_{\max} , and c_{\min} are known, the dependence (14) completely determines the mass-exchange process. If the driving force is a nonlinear function of the concentration c we obtain, in place of (9), another equation which should be solved for appropriate boundary and initial conditions.

NOTATION

$w(\bar{\xi}, t)$, probability density; $\bar{\xi}(t) = \{\xi_1(t), \xi_2(t), \dots, \xi_n(t)\}$, coordinates in the phase space; $k_i(\bar{\xi}, t)$ and $k_{ij}(\bar{\xi}, t)$, drift and diffusion coefficients in the Kolmogorov-Fokker-Planck equation; $F_i(\bar{\xi}, t)$ and $F_i^1(\bar{\xi}, t)$, deterministic and random components on the right-hand side of the kinetic equations; \bar{X} , mass-exchange driving force; \bar{V} and \bar{V}' , average and pulsating velocities; c_i , concentration of i -th component; D_{ef} , effective diffusion coefficient; s_k and v_k , surface area and volume of a particle; I_i , current component; μ_{ji} , chemical potential of component i in phase j ; c_p , c_{\min} , and c_{\max} , equilibrium, minimum, and maximum possible values of the concentration, respectively; σ , intensity of random fluctuations.

LITERATURE CITED

1. P. G. Romankov, N. B. Rashkovskaya, and V. F. Frolov, Mass-Exchange Processes in Chemical Technology [Russian translation], Khimiya, Leningrad (1975).
2. V. I. Klyatskin, Stochastic Equations and Waves in Randomly Inhomogeneous Media [in Russian], Nauka, Moscow (1980).
3. S. Chandrasekar, Stochastic Problems in Physics and Astronomy [Russian translation], IL, Moscow (1947).
4. V. A. Kazakov, Introduction to the Theory of Markov Processes and Some Radiotechnical Problems [in Russian], Sovet-skoe Radio, Moscow (1973).
5. Y. A. Buyevich and I. N. Shchelchkova, "Flow of dense suspensions," Prog. Aerospace Sci., 18, 121-150 (1978).
6. R. I. Nigmatulin, Foundations of the Mechanics of Heterogeneous Media [in Russian], Nauka, Moscow (1978).
7. V. V. Kafarov and I. N. Dorokhov, System Analysis of Processes in Chemical Technology [in Russian], Nauka, Moscow (1976).

8. G. K. Batchelor, "Mass transfer from a particle suspended in fluid with a steady linear ambient velocity distribution," *J. Fluid Mech.*, **95**, 369-400 (1979).
9. A. A. Medvedev, "On the generalized theory of processes in chemical technology," in: *Current Problems in Chemical Technology* [in Russian], Leningrad Technological Inst. (1975), pp. 225-234.
10. N. S. Koshlyakov, É. B. Gliner, and M. M. Smirnov, *Partial Differential Equations of Mathematical Physics* [in Russian], Vysshaya Shkola, Moscow (1970).
11. É. Kamke, *Handbook of Ordinary Differential Equations* [in German], Chelsea Publ.

EQUILIBRIUM AGGREGATION IN A MODERATELY CONCENTRATED FINELY DISPERSED SYSTEM.

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The equilibrium properties of dispersed small interacting particles capable of reversible aggregation are investigated.

The aggregation and structurization of a finely dispersed system can lead to changes in its physical characteristics (effective viscosity, thermal and electrical conductivities, etc.) by more than one or two orders. The shape and structure of the aggregates formed depend on the interaction between the particles of the dispersion, and if the interaction is central fairly coarse aggregates can be regarded as approximately spherical. Below we consider a system of spherical aggregates in a state of detailed balance with one another and with single particles. We ignore the formation of structures by the aggregates, which is possible in a concentrated system. This restricts the analysis to reversible aggregation processes in moderately concentrated systems.

Attempts to apply the techniques of equilibrium statistical mechanics to the investigation of such systems are rather rare [1-6]. The intrinsic volume of the particles is usually ignored in this case [1-5], which does not allow the examination of a highly concentrated system; some critical comments on [1-4] are made in [6]. We adopt here the method of [6], based on the use of a lattice model of the type introduced in [7] and suitable for the analysis of concentrated systems; we also correct the inaccuracies in [6].

General Relations. Assuming that the states of a particle system with different "occupation numbers" v_i are distinguishable, we determine the total number of possible states of the system by the relation [6]

$$W(v_i) = \frac{M!}{(M-N)! N!} \frac{N!}{\prod_i N_i!} \prod_i \frac{N_i!}{(i!)^{v_i} v_i! M^{v_i(i-1)}}, \quad (1)$$

where

$$M = \frac{V}{(v/\rho_a)} = \frac{\rho_a}{\rho} N, \quad N = \sum_i N_i, \quad N_i = i v_i. \quad (2)$$

The first, "configurational," cofactor in (1) is equal to the number of ways in which N indistinguishable particles can be arranged in a lattice with M cells of the same type [7]; the second, "conformational," cofactor represents the number of ways in which N particles can be distributed among "aggregate phases" with N_i particles; the third factor is the number of ways in which the particles of these phases can be distributed among different aggregates, with due allowance for the constraint effects manifested when particles which are not free but are bound into aggregates are arranged in a lattice (see [8] also). In [2] the quantity W was mistakenly identified only with the second cofactor in (1), in [5] the configurational contribution to W was completely ignored, and in [6] the Boltzmann factor

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