CERTAIN PROBLEMS WITH THE APPLICATION OF STOCHASTIC DIFFUSION PROCESSES FOR THE DESCRIPTION OF CHEMICAL ENGINEERING PHENOMENA. DIFFUSIONAL CHANGE OF SOLID PARTICLE SIZE

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To the description of changes of solid particle size in population, the application was proposed of stochastic differential equations and diffusion equations adequate to them making it possible to express the development of these populations in time. Particular relations were derived for some particle size distributions in flow and batch equipments. It was shown that it is expedient to complement the population balances often used for the description of granular systems by a “diffusion” term making it possible to express the effects of random influences in the growth process and/or particle diminution.
Key words: Particle size distribution; Population balances; Stochastic differential equations.

The operations often occur in chemical engineering connected with the solid particle growth (crystallization, polymerization) or with their dimension diminution (grinding, crushing, dissolution). In vast majority of cases, the size change of such particles can be considered as a non-stationary stochastic process leading to their certain distribution both as to their size and as to their shape. In the theoretical description of such systems, the shape factor of a particle of the given population is usually considered unchanging. This assumption makes it possible to choose some particle length dimension to be its basic characteristic. During the above-mentioned operations, even the – in general, random – motion of these particles takes place, so that the further characteristics of the process will be position and momentum of their centre of gravity.

In considerations aiming at practical applications, however, the last two quantities are not, as a rule, considered, and a uniform particle distribution is usually assumed in working space or in the inlet and outlet fluid streams which carry along[1] the particles. The characteristic particle dimension $L(t)$ which may generally be considered as a stochastic time function is then the only defining factor when describing the particle “behaviour”. This linear dimension will be called the particle size in further text. As a general characteristic, distribution function $F(l;t)$ is introduced for the stochastic functions in probability theory as probability **P** that the particle size will be at instant t lower than the given value of variable l,

$$F(l;t) = \mathbf{P}\left\{L(t) < l\right\} \;, \qquad (1)$$

or, as the case may be, the first derivative of this function – the probability density

$$f(l;t) = \frac{\partial F(l;t)}{\partial l} \;. \qquad (1a)$$

The term probability density will sometimes be replaced by the term particle distribution density in further text.

For a fixed time instant $t = t_1$, the distribution function approximates the particle size distribution in some set (population)

$$F^*(l) \equiv F(l;t_1) \approx \frac{N\left\{L(t_1) < l\right\}}{N_T} \qquad \left[N_T \equiv N\left\{L(t_1) < \infty\right\}\right] \;, \qquad (2)$$

i.e., as number N particles smaller than l out of the set considered to the total number N_T of particles in the same set. The relation holds the more accurately the larger is N_T. In this way defined function or its probability density $f^*(l) \equiv dF^*(l)/dl$ is then approximated by some functions derived in the probability theory, or if need be, by some empirical distributions. For the description of stationary distributions of solid particles, one usually employs[1–3] the probability density of normal distribution $f_N(l;\overline{L},\sigma^2)$, of lognormal distribution $f_N(\log l;\log \overline{L}',\log^2 \sigma')/l$, gamma distribution $f_G(l;a/b, \underline{a} + 1)$, from the empirical relations, most often the Rosin–Rammler distribution* $\gamma(l/\overline{L})^{\gamma-1} \exp[-(l/\overline{L})^\gamma]/\overline{L}$.

For the description of development of the solid particle population, Randolph and Larson[4] used the population balance (see also ref.[5]) and derived a first-order partial differential equation whose solution is a so-called solid particle population density,

$$n(l;t) = f(l;t)\,\frac{N_T}{V} \;, \qquad (3)$$

* The distribution parameter designation in this paragraph was taken over from the works cited[1,2]. Functions $f_N()$ and $f_G()$ are defined in the List of Functions.

where V is the suspension volume in the system in which the considered population occurs. Authors[4] showed that under some simplifying assumptions, the population balance for this system can be written in the form

$$\frac{\partial n(l;t)}{\partial t} + \frac{\partial[v(l)n(l;t)]}{\partial l} + \frac{n(l;t)}{\overline{t}} = 0 \ , \qquad (4)$$

where symbol $v(l)$ stands for the rate of change of particle size and $\overline{t}$ the mean residence time of particles in system, if the system considered is flow one (in a non-flow system, evidently, the mean residence time grows limitlessly, and the last term is equal to zero). For constant values of N_T and V, the population density is directly proportional to the probability density of particle size distribution, and Eq. (*4*) is consequently identical even for the function $f(l;t)$.

The aim of this work is the effort to describe the particle size changes from a uniting point of view; we shall consider these changes to be stochastic process of diffusion type (see, e.g. refs[6–8]). We shall show simultaneously that the approach proposed here makes it possible to describe the chronological development of populations, sometimes even only by means of elementary functions. The partial results attained in this direction by other authors will be referred to at the respective places in discussion*.

THEORETICAL

The changes of solid particle size will be described first in a non-flow stirred equipment, i.e., in a bounded system in which the particles can freely move. Let us consider a single particle and accept these assumptions as to the changes of its size:

1. Neither on changing the particle size, nor during its motion, a change of its shape occurs.

2. The particle in the system neither arises, nor decays.

3. The initial particle size is generally random and can be determined by the initial size distribution.

4. The change rate of particle size consists of the deterministic and stochastic contribution; the discrete changes of its size are here excluded. Both the contributions can be generally a function of particle size but not explicitly of time.

The given assumptions determine the size distribution of the particle considered at any time instant count from the beginning of process. From the law of averages follows that this distribution makes it possible to describe the size distribution of particles of

* The paper submitted has largely the formal mathematical character. Therefore, hereinafter we shall not judge, e.g., the physical meaning of particular parameters in relations written.

identical shape the more accurately the greater the population of these particles is. The given assumptions, therefore, make it possible to determine the particle size distribution of this population.

The first assumption defines the shape invariability of the particle. According to the second assumption, the processes of arising and decaying the particle are excluded. This limitation requires the initiation of the process of particle growing by "seeding". The distribution of "seeding" particles, i.e., the initial size distribution density is determined by the third assumption. (As the initial distribution we shall often consider even the set of particles of a single negligibly small – i.e., practically zero – size.) The fourth assumption excludes step changes of size, therefore, the processes of agglomeration or, on the contrary, disaggregation. Random changes in size are then only of "diffusional" character and are determined by the so-called Wiener process (see, e.g. refs[6–8]). This assumption requires as well that the conditions under which the change of particle size occur (e.g., the stirring intensity) should not change in time during the process. In opposite case, both the above-mentioned rate contributions might be an explicit function of time.

On the basis of the above-mentioned assumptions, it is possible to describe the stochastic change of particle size $L(t)$ in terms of the so-called stochastic differential equation[6–8]

$$\mathrm{d}L(t) = v[L(t)]\,\mathrm{d}t + w[L(t)]\,\mathrm{d}W(t) \quad , \tag{5}$$

where the first term on the right-hand side stands for the deterministic and the second term the stochastic contribution to the particle size change. Symbol $W(t)$ stands for the Wiener process (see, e.g. ref.[6]), which is a stochastic function of time with normal distribution, zero expected value and the dispersion equal to time interval from the beginning of process[6]. Ordinates of this process can, with the same probability, take positive and negative values. This property sets certain limits to the coefficients in Eq. (*5*): They must be apparently such that the length dimension of particle should have a positive value at each instant.

In the literature (see, e.g. refs[6,7]), a so-called transitive probability density $f_t(l;t|l_p;t_p)$ is defined for process $L(t)$ which characterizes the probability that the particle size will have a value near to l at instant t on condition that at the initial instant $t = t_p$, it was equal l_p. It is proved there that function $f_t()$ is the solution of the partial differential equation

$$\frac{\partial f_t}{\partial t} + \frac{\partial[v(l)f_t]}{\partial l} - \frac{1}{2}\frac{\partial^2[w^2(l)f_t]}{\partial l^2} = 0 \quad . \tag{6}$$

This equation requires generally one initial and two boundary conditions in interval $0 \le l < \infty$. For the upper limit of the interval, the condition $\lim_{l\to\infty} f_t(l;t|l_p;t_p) = 0$, which means that the particle size is not generally limited from above, however, the probability of its growth ad infinitum is zero. In case of the lower limit (i.e., for $l = 0$), the situation is more complicated. Gichman and Skorokhod[8] affirm that in case of a so-called natural boundary (that is such which cannot be reached by the given process), conditions $w(0) = 0$ and $v(0) \ge 0$ have to hold here for coefficients of Eq. (*5*).

In agreement with the Feller theory[9,10], it is not necessary to consider the boundary conditions at all in case of the natural boundary for process $L(t)$ is not able to reach this boundary and consequently $\lim_{l\to 0+} f_t(l;t|l_p;t_p) = 0$. However, from this theory simultaneously follows that for the non-zero value of probability density at point $l = 0$ (i.e., for null particle size – this situation may occur above all when $w(0) = 0$ and $v(0) = 0$), the situation is not so simple. The boundary condition for $l = 0$ will then depend on the actual form of coefficients $v(l)$ and $w(l)$.

In our further considerations, we shall mostly assume the natural boundaries. The opposite case (i.e., other type of bounds at point $l = 0$) will be always discussed separately, by the term zero-size particle being understand the particle whose dimensions are negligibly small.

The initial condition is in agreement with the third assumption given and it may be generally written in the norm form as the probability density $f_p(l_p;t_p)$ which gives the initial particle distribution. For a non-flow system we shall always consider that $t_p = 0$ and omit this designation in further records, i.e., we shall write, e.g., $f_p(l_p;0) = f_p(l_p)$. Equation (*6*) is linear with respect to $f_t()$, and its solution will be therefore as well the integral

$$f(l;t) = \int_0^\infty f_t(l;t \mid l_p)\, f_p(l_p)\, \mathrm{d}l_p \quad . \tag{7}$$

The probability densities in this equation may be understood in this way: Function $f_t()$ gives the particle distribution at instant t on the assumption that at the initial (zero) instant, they all were of the same size l_p. Function $f()$ characterizes their distribution at instant t for the case when their initial distribution is given by function $f_p()$. For values t growing ad infinitum (i.e., practically for a great time interval elapsing from the beginning of the process), it is possible to determine the stationary distribution (as far as such a distribution exists) by the relation

$$f_s(l) = \lim_{t\to\infty} f(l;t) \quad . \tag{8}$$

Let us go over to the case of flow system and complement the above-mentioned assumptions with others:

5. The number of particles passing throug the system along with the entraining liquid is invariable in time. The distribution of their sizes $f_{fp}(l_p)$ at the system inlet is not a function of time.

6. The particle residence time in the system, i.e., time interval Δt between the moments of input and output, is, in general, a stochastic quantity whose probability density $f_f(\Delta t)$ is given and does not vary with time.

The two assumptions along with assumption *4* express the fact that the system functions under steady conditions, as a matter of fact, above all at constant medium flow rate, and under constant stirring regime. The coefficients in Eqs (*5*) and (*6*) will therefore be nor in this case an explicit function of time, and as far as the operation conditions in the flow and non-flow system considerably do not differ, they may be for both these cases considered identical.

In the theory of stochastic processes[8], it is further proved that unless the above-mentioned coefficients are functions of time, the transitive probability density has a stationary form to the effect that it does not depend on time instants t and t_p individually but only on their difference: $f_t(l;t|l_p;t_p) = f_t(l;t - t_p|l_p) = f_t(l;\Delta t|l_p)$.

On the basis of these considerations and on the assumption that the initial distribution in the non-flow and the inlet distribution in the flow system are identical (i.e., that $f_p(l_p) \equiv f_{fp}(l_p)$), the function $f(l;\Delta t)$ defined by Eq. (*7*) can be understood as the probability density characterizing the distribution of particles leaving the system with the same residence time Δt.

The density of particle size distribution in the outlet stream $f_e(l)$ are then determined in terms of a so-called randomization of time parameter (see, e.g. ref.[11])

$$f_e(l) = \int_0^\infty f(l;\Delta t)\, f_f(\Delta t)\, \mathrm{d}\Delta t \ , \qquad (9)$$

where $f_f(\Delta t)$ is the probability density of residence time distribution in flow system.

The procedure outlined makes it possible to compute generally the particle distribution in flow system; we shall show in Discussion that it is, in a certain respect, a generalization of population balance (*4*). The particular form of the coefficients in Eq. (*5*) has to be chosen on the basis of physical insights into the given process. The general solutions of corresponding Eq. (*6*) under the suitably chosen initial and boundary conditions, or if need be, the subsequent randomization (*9*) are, of course, sufficiently complicated, and therefore it is usually necessary to employ suitable numerical methods. In next paragraph, however, we shall show that some distributions used in practice or at least lower moments of these distributions can be obtained by analytical procedures.

Particular Relations for Particle Distribution in Non-Flow System

Further we shall present only such distribution densities of solid particle or moments of these distributions which may be expressed in terms of elementary functions. The derivations of some relations and the results which contain higher transcendental functions are given in Appendix.

In concretizing the form of coefficients in Eq. (*5*), we shall assume that they are such that they are, either in Eq. (*5*) or in Eq. (*6*), a linear function of particle size. Equation (*5*) takes then the form

$$\mathrm{d}L(t) = (\alpha - \beta L(t))\,\mathrm{d}t + \kappa_{2q}[L(t)]^q\,\mathrm{d}W(t) \qquad [q = 0, 1/2, 1]\ . \tag{10}$$

From the discussion of boundary conditions of Eqs (*5*) and (*6*) it follows that it is necessary to delimit the range of validity of coefficients α, β, and κ_{2q} in Eq. (*10*). The requirement of natural boundaries for $L(t) = 0$ leads to these conditions

$$\alpha \geq 0\ ;\ \ -\infty < \beta < +\infty\ ;\ \ \kappa_0 = 0\ ;\ \ -\infty < \kappa_1, \kappa_2 < +\infty\ . \tag{11}$$

Further we shall show that only some combinations of these parameters are suitable for the description of changes of particle size. From Eqs (*5*) and (*6*) follows that the partial differential equation for transitive probability density* $f_t(l;t\,|\,l_p)$,

$$\frac{\partial f_t}{\partial t} + \frac{\partial[(\alpha - \beta l)f_t]}{\partial l} - \frac{1}{2}\,\kappa_{2q}^2\,\frac{\partial^2(l^{2q}f_t)}{\partial l^2} = 0 \tag{12}$$

corresponds to relation (*10*).

It is apparent that Eq. (*10*) is linear with respect to particle size for $q = 1$, Eq. (*12*) on the contrary for $q = 1/2$. Solution of the last relation results in the expressions for time development of particle distribution density. A considerable part of information – frequently sufficient – however, can provide even simpler equations describing the time development of moments of this distribution. The expected (average) value of particle size and the dispersion (variance) around this average value are concerned. The corresponding procedures were dealt with in the chemical-engineering literature by, e.g.,

* Functions f_t obviously depend as well on the value of parameter q, and it would be therefore necessary to distinguish them by different symbols. However, we shall not do so because it will be clear from the context which value of this parameter will be concerned.

King[12]. To obtain the relation for the first moment, i.e., the mean value, Eq. (*12*) is multiplied by variable l and then integrated by parts with respect to this variable within limits from zero to infinity. We obtain the ordinary differential equation

$$\frac{\mathrm{d}\overline{l(t)}}{\mathrm{d}t} + \beta\overline{l(t)} - \alpha = 0 \quad , \tag{13}$$

where $\overline{l(t)}$ denotes the mean value of distribution. The solution of Eq. (*13*) is given by the relation

$$\overline{l(t)} = \overline{l}_\mathrm{s}[1 - \Theta] + \overline{l}_\mathrm{p}\Theta \quad , \tag{14}$$

where $\overline{l}_\mathrm{p} \equiv \overline{l(0)}$ and $\overline{l}_\mathrm{s} \equiv \overline{l(\infty)} = \alpha/\beta$ are the mean values of the initial or stationary distribution and $\Theta \equiv \exp(-\beta t)$. It follows from Eq. (*14*) that for negative values of β, the mean value of particle size diverges and the distribution consequently will not have a stationary solution. The same holds for null value of β; the growth of mean value is, however, substantially slower

$$\overline{l(t)} = \alpha t + \overline{l}_\mathrm{p} \qquad [\beta = 0] \quad . \tag{14a}$$

In case of the null value of α (and positive β), the mean value of stationary solution is equal zero. It is evident that the relations for the first moment do not depend on the value of parameter q and consequently nor on κ_{2q}.

Analogously we obtain the differential equation for the second moment, relation (*12*) has to be multiplied by l^2 in this case

$$\frac{\mathrm{d}\overline{l^2(t)}}{\mathrm{d}t} - 2\alpha\overline{l(t)} + 2\beta\overline{l^2(t)} - \kappa_{2q}\overline{l^{2q}(t)} = 0 \quad . \tag{15}$$

Symbol $\overline{l^2(t)}$ denotes a so-called second moment round origin. Of greater significance is the second central moment, i.e., variance $\sigma^2(t)$

$$\sigma^2(t) = \overline{l^2(t)} - \overline{l(t)}^2 \quad . \tag{16}$$

For the forms of coefficients considered by us, it is possible to write down directly the differential equation for the variance if Eq. (*13*) is multiplied by $\overline{l(t)}$ and the relation obtained in this way is subtracted from Eq. (*15*),

$$\frac{\mathrm{d}\sigma^2(t)}{\mathrm{d}t} + 2\beta\sigma^2(t) = \kappa_{2q}^2\overline{l^{2q}(t)} \quad . \qquad (17)$$

The solution of this relation as well as the solution of Eq. (*12*) depends on the value of parameter q (the solution of Eq. (*12*) is given in Appendix in more detail). Therefore we are writing here the results for each value of q separately along with the resultant relations for density of solid particle distribution as far as they may be written in terms of elementary functions and we shall show that each of values q leads to another type of distribution.

Normal Distribution (q = 0)

According to conditions (*11*), parameter κ_0 may take only null value. A non-zero value of this parameter, however, leads to the often used normal distribution, and therefore it will be generally considered here as well. As it will be shown in Discussion in more detail, use of an incorrect (i.e., non-zero) value of parameter κ_0 admits the possibility of existence of negative particle size.

Solving Eq. (*17*) for $\kappa_0 \neq 0$, we get the relation

$$\sigma_0^2(t) = \sigma_{0\mathrm{s}}^2[1 - \Theta^2] + \sigma_\mathrm{p}^2\Theta^2 \quad , \qquad (18)$$

where $\sigma_{0\mathrm{s}}^2 \equiv \sigma_0^2(\infty) = \kappa_0^2/2\beta$ denotes the stationary variance and σ_p^2 the variance at initial instant. The respective distribution density was derived by Uhlenbeck and Ornstein (cited according to ref.[10]) in the form

$$f(l;t) = f_\mathrm{N}[l;\overline{l(t)},\sigma_0^2(t)] \qquad (19)$$

which is the probability density of normal (Gauss) distribution, whose parameters $\overline{l(t)}$ and $\sigma_0^2(t)$ defined by Eqs (*14*) and (*18*) change generally with time. We considered here that the initial distribution is also normal with parameters $\bar{l}_\mathrm{p}$ and σ_p. It is apparent that for long time intervals from the beginning of the process, function $f()$ converges to the stationary density of distribution $f_\mathrm{s}(l) = \lim_{t\to\infty} f(l;t)$.

For the only admissible value of parameter $\kappa_0 = 0$ (and at null initial variance), $\sigma_0(t)$ is identically equal zero, and the probability density $f(l;t)$ converges to the so-called Dirac function

$$f(l;t) = \delta[l - \overline{l(t)}] \qquad [\kappa_0 = 0] \ , \tag{20}$$

which takes the null values for every l except the value $\overline{l(t)}$ when it grows ad infinitum. Such a function describes the population of particles which were at the beginning of the same size l_p, and this size changes with time, however, it is the same* for all particles at every time instant.

Gamma Distribution ($q = 1/2$)

By solving Eq. (*17*), we obtain in this case, after rearranging, the expression for variance as a function of time:

$$\sigma_1^2(t) = \overline{l(t)}^2/b + [\sigma_p^2 - \overline{l}_p^2/b] \ , \tag{21}$$

where the average value $\overline{l(t)}$ is defined by Eq. (*14*) and $b \equiv 2\alpha/\kappa_1^2$. Relation (*21*) is especially simplified when the expression in square brackets is equal zero. In this case the ratio of variance and square of mean value (i.e., square of variation coefficient) does not depend on time. The relation for the distribution density is as well relatively simple in this case,

$$f(l;t) = f_G[l;b/\overline{l(t)},b] = \frac{b}{\overline{l(t)}\Gamma(b)}\left(\frac{bl}{\overline{l(t)}}\right)^{b-1} \exp\left(-\frac{bl}{\overline{l(t)}}\right) . \tag{22}$$

Function $f(l;t)$ is the probability density of gamma distribution whose mean value is a function of time. In case that the expression in parentheses in Eq. (*21*) is not equal zero, function $f()$ is more complicated; its form and derivation are given in Appendix. It is apparent from Eq. (*22*) that for values $b > 1$, i.e., $2\alpha > \kappa_1^2$, the probability of occurrence of negligibly small particles is very little; in case $b = 1$, however, function $f(l;t)$ has finite and for $b < 1$ even infinite value when converging l to zero. In these two cases, it is not possible, according to Feller[9], to consider the limit at point $l = 0$ as natural.

* Function $\delta(l)$ expresses the distribution of particles of negligible (theoretically null) dimension.

The case when parameter α in Eqs (*10*) or (*12*) equals zero, was analyzed by Feller (cited according to ref.[10]). The probability density $f(l;t)$ is for this case expressed, as it will be given in Appendix, in terms of the modified Bessel function.

Lognormal (and Other) Distributions ($q = 1$)

The expression for variance as solution of Eq. (*17*) is generally rather complicated and will not be given here. We have not succeded to find the expression for the probability density $f(l;t)$ in simple analytical form. However, it is possible to write down such a relation for stationary distribution according to Eq. (*8*) by solving Eq. (*12*) for $\partial f/\partial t \equiv 0$ (see ref.[13])

$$f_s(l) = \frac{f_G[1/l;a\bar{l}_s,a+1]}{l^2} \quad , \tag{23}$$

where $a \equiv 2\beta/\kappa_2^2$ and $\bar{l}_s = \alpha/\beta$. Equation (*23*) describes the gamma distribution, however, with reciprocal argument (see also refs[1,14]). The expression holds only for positive values of parameter β.

The analytical expression for the population development in time can be found in the particular case of $\alpha \equiv 0$. It is possible to show (see Appendix) that in this case the population is characterized by the lognormal distribution

$$f(l;t) = f_N[\log(l); \log[\overline{l(t)}/r(t)], \log r^2(t)]/l \quad , \tag{24}$$

where $r^2(t) \equiv [(\sigma_p^2 + \bar{l}_p^2)/\bar{l}_p^2] \exp(\kappa_2^2 t)$ and $\overline{l(t)} = \bar{l}_p \exp(-\beta t)$. The variance is, for this case, given by the relation

$$\sigma_2^2(t) = \sigma_p^2 \exp[-(2\beta - \kappa_2^2)t] + \bar{l}_p^2 \exp(-2\beta t)\,[\exp(\kappa_2^2 t) - 1] \quad . \tag{25}$$

For the case of diminishing the particles, the relation $2\beta > \kappa_2^2$ has to hold.

Particular Relations for Particle Distribution in Flow System

General relation for the particle size distribution in flow system is expressed by relation (*9*). Different particular expressions for function $f(l;\Delta t)$ behind the symbol of integral are given by Eqs (*19*), (*20*), (*22*) and (*24*), everywhere inserting symbol Δt for t as it follows from the consideration before Eq. (*9*). Function $f_f(\Delta t)$ stands for the probability density of residence times in flow system. Comparatively extensive literature (see, e.g.

refs[15,16]) is bestowed on this question in which a great number of relations is proposed for expressing function $f_f()$. Here we shall consider only the gamma distribution[15] of residence times of particles in flow system

$$f_f(\Delta t) = f_G(\Delta t; c/\overline{t}, c) \quad , \tag{26}$$

i.e., the equation analogous to Eq. (*22*). Symbol $\overline{t}$ denotes the mean residence time of particles in system. Symbol c is the distribution parameter and its value decreases with increasing the intensity of randomness of particle motion [$c \geq 1$]. We have shown previously[13] that this function can be obtained on the basis of concepts on random particle motion in flow system which lead to the stochastic differential equations analogous to the relations given in this contribution. According to our experience, function (*26*) makes it possible to describe well the experimental data on the liquid residence times in homogeneous system[17].

Inserting this relation into Eq. (*9*) results in expressions which, in most cases, have to be integrated numerically, analytically can be usually described only the moments of resulting distribution $f_e(l)$.

In case that the density of particle size distribution is given by Eq. (*22*), we shall obtain, for the mean size value of particles leaving the flow system, the relation

$$\overline{l}_e = \overline{l}_s + (\overline{l}_p - \overline{l}_s)\mu_1 \quad , \tag{27}$$

where the expressions for the stationary and initial (here entering) mean values have been defined at Eq. (*14*) and $\mu_1 \equiv [c/(c + \beta\overline{t})]^c$. The relation for variance is more complicated

$$\sigma_e^2 = \overline{l}_e^2/b + (\overline{l}_p - \overline{l}_s)^2(\mu_2 - \mu_1^2)[1 + (1/b)] + \mu_2(\sigma_p^2 - \overline{l}_p^2) \quad ; \tag{28}$$

the expression for parameter b has been defined at Eq. (*21*). Further, $\mu_2 \equiv [c/(c + 2\beta\overline{t})]^c$.

For the value of parameter $c = 1$, these expressions are simplified. In this case, the distribution of residence times is described by the exponential function

$$f_t(\Delta t) = f_G(\Delta t; 1/\overline{t}, 1) = \frac{1}{\overline{t}} \exp(-\Delta t/\overline{t}) \quad ; \tag{29}$$

the flow system therefore behaves as an ideal mixer with the mean residence time $\overline{t}$. Moreover, if we consider that particles of negligibly small size enter the system (their distribution density is described by the Dirac function $f_{fp}(l_p) = \delta(l_p)$), it is possible to write, for the distribution density of particles leaving the system, the differential equation describing even the non-stationary regime of the particle size change (see Appendix)

$$\frac{1}{2}\frac{\partial^2[w^2(l)\, f_e(l;t)]}{\partial l^2} - \frac{\partial[v(l)\, f_e(l;t)]}{\partial l} - \frac{f_e(l;t)}{\overline{t}} = \frac{\partial f_e(l;t)}{\partial t} \quad . \qquad (30)$$

The stationary particle distribution density at the system outlet, i.e., $f_e(l) = \lim_{t\to\infty} f_e(l;t)$, can be obtained as a solution of ordinary differential equation which we obtain so that $\partial f_e(l;t)/\partial t \equiv 0$ is set in Eq. (*30*). It is shown in Appendix that for $t \to \infty$, the solution of the ordinary differential equation obtained in this way, is identical with the solution of integral (*9*) where we insert from Eq. (*29*) for $f_t(\Delta t)$. For the case when the particular form of coefficients in Eq. (*10*) leads in the non-flow system to gamma distribution (i.e., for value $q = 1/2$), this equation can be written in the form

$$\frac{1}{2}\kappa_1^2\frac{d^2(lf_e)}{dl^2} - \frac{d[(\alpha - \beta l)f_e]}{dl} - \frac{f_e}{\overline{t}} = 0 \quad , \qquad (31)$$

and its solution in terms of integral (see Appendix) is

$$f_e(l) = \frac{\lambda h}{\Gamma(b)}\int_{\lambda l}^{\infty} \exp(-u)u^{b-h-1}(u - \lambda l)^{h-1}\, du \quad , \qquad (32)$$

where $\lambda \equiv 2\beta/\kappa_1^2$, $b \equiv 2\alpha/\kappa_1^2$, $h \equiv 1/(\beta\overline{t})$.

The simplest way when it is possible to describe function $f_e(l)$ in terms of elementary functions is this one when the subintegral function $f(l;t)$ in Eq. (*9*) is equal to the Dirac function, introduced by relation (*20*). If we, moreover, insert here for the mean value from Eq. (*14a*) for $l_p = 0$, we obtain

$$f_e(l) = \int_0^{\infty} \delta[l - \alpha\Delta t]\, f_G(\Delta t;c/\overline{t},c)\, d\Delta t = f_G(l;c/\overline{t}\alpha,c) \quad ; \qquad (33)$$

the density of particle distribution is then again described by the gamma distribution. Parameters of this distribution are, however, in this case determined above all in terms of parameters of distribution of particle residence times[1].

RESULTS AND DISCUSSION

It was shown in theoretical part that the approach proposed in this work, i.e., use of stochastic differential equations (SDE) and the adequate diffusion equations for modelling the diffusion changes of particle size, makes it possible to derive some distributions used for the description of particle distribution (see Table I). In doing so, above all the equations were presented making it possible to describe relatively simply the evolution of these distributions in time.

Use of SDE makes it possible to express simply appropriate physical concepts on stochastic change of particle size. It has been emphasized that the quantitative formulation of these concepts has to meet requirements of a so-called natural boundary condition for null (or negligibly small) particle size: The deterministic component of rate of the particle size change for this limiting value has not to be negative and its random component has to be equal zero.

The possibility of using SDE for the description of crystal size was outlined by Buyevich et al.[18] when analysing the non-stationary behaviour of flow crystallizers. The adequate diffusion equation had already been written down, substantially formerly by Randolph and White[1,19]. In the works cited, however, the "diffusion coefficient" (here designated by expression $w^2(l)/2$) was considered to be a positive constant, therefore a quantity independent of particle size. As it follows from comparison of Eqs (*6*) and (*12*), for the null value of parameter q, $w^2(l) = \kappa_0^2 = \text{const} > 0$ will in this case hold.

In the paragraph on normal distribution (q = 0), however, we have said that its use for the description of particle size distribution (see Eq. (*9*)) is theoretically incorrect for it predicts the existence of particles with "negative" size. This fact manifests itself especially significantly when describing the growth of particles with negligibly small size at the beginning of the process.

The portion of "negative" particles $p(t)$ at each time instant may be expressed by the relation

TABLE I
Types of particle size distribution in dependence on the form of coefficients of stochastic differential equation (*10*)

Values of coefficients of SDE (*10*)			Type of distribution	Note/Range of validity
q	α	β		
0	>0	>0	normal	theoretically incorrect, even "negative" particle sizes considered
1/2	>0	>0	gamma	$\sigma_p^2 - l_p^2\,\kappa_1^2/2\alpha = 0$
1	>0	>0	gamma with reciprocal argument	stationary distribution only
1	0	>0	lognormal	$l_p > 0$

$$p(t) = \int_{-\infty}^{0} f(l;t)\, \mathrm{d}l = \int_{-\infty}^{0} f_{\mathrm{N}}(l;\overline{l(t)};\sigma_0^2(t))\, \mathrm{d}l \ , \tag{34}$$

where it is necessary to solve the integral numerically or on using the tabulated values of the Laplace function[20].

Quantity $p(t)$ will have null value only in case of $\kappa_0^2 \equiv 0$, i.e., for only one admissible value of parameter κ_0 when the probability density $f(l;t)$ can be expressed by means of Eq. (*20*). In this case the change of particle size is strictly deterministic. This requirement is fulfilled, at least approximately, for a very low value of variation coefficient[1]. It is, however, evident that for the description of time evolution of particle distribution with the initial negligibly small size, a low value of this coefficient can be reached only after a sufficiently long time interval from the beginning of the process.

This assertion is illustrated in Figs 1. Figure 1*a* illustrates the time development of population which has normal distribution at negligibly small initial particle size. Figure 1*b* shows portion $p(t)$ of "defective" particles (i.e., the particles which would have negative size). The same time instants for which the distribution densities are illustrated in Fig. 1*a*, are here marked with solid points*.

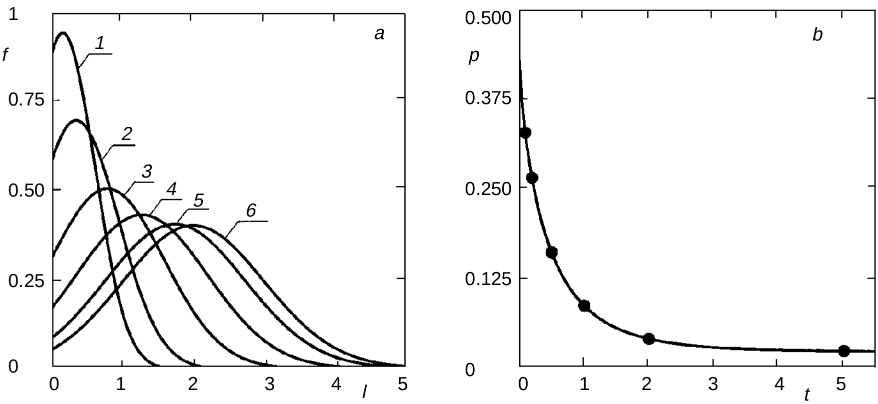

FIG. 1

Normal particle size distribution. Parameters: $\alpha = 2$, $\beta = 1$, $\kappa_0 = \sqrt{2}$, $q = 0$, $l_p = 0$, $\sigma_p = 0$. *a* Particle growth in time t according to Eq. (*19*); *1* $t = 0.1$, *2* $t = 0.2$, *3* $t = 0.5$, *4* $t = 1$, *5* $t = 2$, *6* $t = 5$. *b* Portion of particles with "negative" size according to Eq. (*34*). Points designate portions of particles for time instants corresponding to curves in Fig. 1*a*

* The values of parameters in these and all further figures were chosen for the depicted dependences to be as illustrative as possible, without, e.g., showing realistically the real size of particles. For this reason we do not give the units of these parameters in figure captions.

The lognormal distribution, which is often considered to be only empirical, does not suffer from this defect, i.e., from predicting the negative values of particle size. However, already Kolmogorov[21] had shown on the basis of stochastic approach to the description of particle disintegration (e.g., grinding) that the density of their size distribution may be expressed in terms of lognormal distribution which will be written down here by the relation

$$f(l;t) = f_{\mathrm{N}}(\log (l);Pt,Q^2t)/l \ . \tag{35}$$

It is reported[3] that this distribution safisfactorily describes the experimental data for sufficiently long time intervals t from the beginning of the process. Reason of this limitation of validity follows from the comparison of distribution parameters in Eq. (*35*) with those of our proposed relation (*24*). As it is stated in Appendix, Eq. (*35*) holds only in case that for Eq. (*24*), the non-equalities are fulfilled

$$\kappa_2^2 t >> \log (\sigma_{\mathrm{p}}^2/\bar{l}_{\mathrm{p}}^2 + 1) \ ; \quad \left|(\beta + \frac{1}{2}\kappa_2^2)t\right| >> \log [(\bar{l}_{\mathrm{p}}^2/(\sigma_{\mathrm{p}}^2 + \bar{l}_{\mathrm{p}}^2)^{1/2})] \ , \tag{36}$$

i.e., for such values of t when it is possible to neglect the effect of parameters of initial distribution (then, obviously, $P = -(\beta + 1/2\kappa_2^2)$ and $Q = \kappa_2$)). Equation (*24*) proposed by us can therefore be considered more general than the distribution proposed by Kolmogorov.

The lognormal distribution proposed here is not too suitable for describing the particle growth, i.e., for the case when $\beta < 0$ (and $\alpha = 0$) for, as it is evident from relations (*14*) and (*25*), its parameters diverge with time. It does not make it possible to describe the growth of particles of negligibly small size as well. As one can see from Eq. (*10*), the contributions $\mathrm{d}L(t)$ for particle size $L(t) \to 0$ are negligibly small as well.

The proposed distribution density (Eq. (*24*)) is, however, suitable for the description of diminishing the particles (at $\alpha = 0$ and $\beta > 0$) for still at the validity of condition $2\beta > \kappa_0^2$ (see note under Eq. (*25*)), it converges with increasing time to the stationary solution – the Dirac function $\delta(l)$, i.e., it expresses the fact that all the particles will, after elapsing a very long time from the beginning of process, negligibly small.

In Fig. 2, the time course is shown of diminishing the particles from the initial distribution density represented by the curve for $t = 0$.

The gamma distribution is free from the failures which were pointed out with the two above-mentioned distributions. The solution of Eq. (*12*) for the value of parameter $q = 1/2$ results, admittedly, generally in higher transcendental functions (see relations (*A8*) or (*A9*) in Appendix), however, it is necessary to emphasize that in case of negligible initial particle dimensions, the solution has always the analytical form of probability density of gamma distribution (whose parameters, however, change with time) for any further time instant (see Eq. (*22*). In case that the initial particle distribution is gamma distribution with the given parameters, the process of changes of particle size must be conducted so that the variation coefficient of distribution should remain unchanged. Examples of the time change of particle density during their growth from a negligible value are given in Fig. 3*a*. The curve for $t = 8$ represents practically stationary distribution.

It is still necessary to point out the fact that the gamma distribution is able to describe even a non-zero probability density (in case of parameter $0 < b \leq 1$) for particles of negligible dimensions. Further it is known that according to central limiting theorem, the form of gamma distribution for high values of parameter b approaches the normal distribution[11]. On the other hand, when value of b approaches unity (from the right), it is possible, by means of the gamma distribution, to approximate the experimental Rosin–Rammler distribution[2], where $\gamma = 1 + \varepsilon$:

$$f(l) = \lim_{\varepsilon \to 0+} (1 + \varepsilon)(l/\bar{l})^{\varepsilon} \exp\left[-(l/\bar{l})^{1+\varepsilon}\right]/\bar{l} \quad . \tag{37}$$

It should be noted here that by the substitution of the independent variable in Eq. (*22*) with its γ-th power and after some rearrangements we obtain a relation for the transitive probability density function of the particle size in the form $f(l;t) = f_G(x;1,b)\,|\,dx/dl|$. The dimensionless variable x is a function of the particle size l and time t

$$x = x(l,t) \equiv \frac{(l/l_s)^{\gamma}[\Gamma(b + 1/\gamma)/\Gamma(b)]^{\gamma}}{[(l_p/l_s)^{\gamma} - 1]\,\Theta + 1} \quad . \tag{38}$$

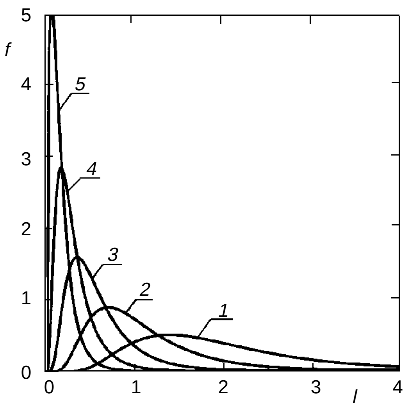

FIG. 2
Density of lognormal distribution of particle sizes – diminishing particles in time t according to Eq. (*24*). Parameters: $\alpha = 0$, $\beta = 3$, $\kappa_2 = 0.5$, $q = 1$, $l_p = 2.01$, $\sigma_p = 1.07$; *1* $t = 0$, *2* $t = 0.2$, *3* $t = 0.4$, *4* $t = 0.6$, *5* $t = 0.8$

At certain values of the parameters γ and b, the preceding relation can be simplified and the function $f(l;t)$ enables (in an analytical form) to describe time evolution of some particle size distributions (most of them were already discussed in this paper):

1. $\gamma = 1$ the gamma distribution,

2. $b = 1$ the Rosin–Rammler distribution,

3. $\gamma = -1$ the gamma distribution with reciprocal argument,

4. $\gamma = 2$, $b = 1$ Raleigh distribution[22].

The solution of Eq. (*12*) for $q = 1/2$ and for the case when parameter α is equal zero (thus, for a negative value of rate of change of particle size $v(l) = -\beta l$, where $\beta > 0$), is to be expressed by means of the modified Bessel function. It may be used even for the case of diminishing the population, i.e., e.g., for dissolving particles. It is so because this solution does not keep norm as it is apparent after its integration over the entire range of variable l (see Appendix)

$$\int_0^{\infty} f_t(l;t\,|\,l_p)\,\mathrm{d}l = 1 - \exp\left[-\frac{\lambda l_p \Theta}{(1-\Theta)}\right] , \qquad (39)$$

where l_p is the initial size of all particles. The value of this integral from the transitive function should be equal unity, which would physically mean that the number of particles of population does not vary during the process. In this case the size of population decreases with time*. The boundary condition for $l = 0$ is here a so-called absorbing boundary[9,10].

The function which describes gamma distribution – see Eq. (*22*), is very flexible and can easily be, e.g., modified for expressing distributions determined experimentally by sieve analysis. Multiplying the probability density by the third power of variable l used for the description of so obtained experimental data, does not change in principle the analytical form of the function[1]. Therefore, it is possible, at least from theoretical point of view, to recommend the gamma distribution as very suitable for the description of particle distribution and its time changes.

The record of changes of particle size in terms of stochastic differential equation (*5*) is suitable also for direct stochastic modelling of the process, as it is apparent from Fig. 3*b*. In this figure, the courses of the same functions are depicted as in Fig. 3*a*, however, they are obtained by numerical modelling of the processes according to stochastic differential equation (*10*) with the value of parameter $q = 1/2$.

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* As far as the initial particle size is determined by gamma distribution, i.e., $f_p(l_p) = f_G(l_p;b/\bar{l}_p,b)$, we obtain the expression $1 - [\lambda \bar{l}_p \Theta/(1-\Theta)b + 1]^{-b}$ by integrating the product of $f_p()$ and the right-hand side of Eq. (*39*) with respect to l_p on the interval $[0,\infty)$. Even in this case the diminution of number of particles therefore takes place.

The problems connected with this way of calculating the probability density of stochastic functions, above all in case when coefficient *w*() in the stochastic term depends on the sought stochastic function *L*(*t*) had been discussed formerly[23,24]. In our case we have used the simplest – Euler – method of integration of the following equation

$$\Delta L(t) = [\alpha - \beta L(t)]\,\Delta t + \kappa_1 [L(t)]^{1/2}\,\Delta W(t)\ \ . \qquad (40)$$

For the time step $\Delta t = k$, the increment of the Wiener process was expressed by the relation $\Delta W(t) = G_{01}\sqrt{k}$, where G_{01} is the stochastic quantity normally distributed with null expected value and unit variance. It was generated by means of the same random number generator as in previous paper[23]. 2^{19} trajectories of random process *L*(*t*) with time step $k = 0.0001$ were calculated.

The outlined approach will be of significance above all in the case when it is necessary to consider even the processes of agglomeration, or diseggregation of particles (i.e., the case when the particle size changes in steps). Then it would be necessary to complement the stochastic differential equation by another random term containing the generalized Poisson process[8] which describes these step changes. Even in this case it is possible to write down the adequate integral-differential equation[8] for the sought density of particle size distribution, its analytical solution, however, is not usually possible. Rather a different approach to this problems (simulation by the Monte Carlo method) is reported by Ramkrishna[5,25].

Further it was shown that as far as the time development of particle population in non-flow system is known, the particle size distribution in a flow system is to be deter-

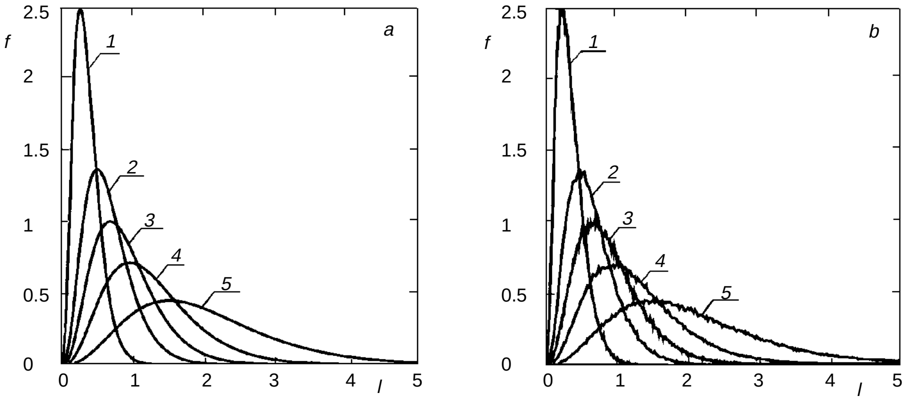

FIG. 3

Density of gamma distribution of particle sizes – particle growth in time *t*. Parameters: $\alpha = 2$, $\beta = 1$, $\kappa_1 = 0.5$, $q = 1/2$, $l_p = 0$, $\sigma_p = 0$; *1* $t = 0.2$, *2* $t = 0.4$, *3* $t = 0.6$, *4* $t = 1$, *5* $t = 8$. *a* In terms of Eq. (*22*), *b* stochastic modelling according to Eq. (*40*) mined to advantage by means of randomization of time variable (see Eq. (*9*)) on the assumption that the residence time distribution of particles in the system is known as well.

In case the density of particle size distribution in non-flow system is described by the gamma distribution, and the flow mixer is ideally stirred, Eq. (*32*) was derived. It is possible to prove (see Appendix) that providing the values of parameters β and κ_1 in this relation approach zero so that simultaneously λ remains a positive constant, the expression on the right-hand side of Eq. (*32*) converges to function $f_G()$ in Eq. (*33*) for $c = 1$, i.e., for the exponetial distribution of particle sizes

$$f_e(l) = \frac{\exp(-l/\bar{t}\alpha)}{\bar{t}\alpha} \qquad [c = 1] \ . \tag{41}$$

It might be shown as well that for non-zero values of parameters κ_1 and β ($\beta > 0$), an "excess" of particles of small sizes takes place with respect to the number of small particles calculated by means of Eq. (*41*) in case $h > b - 1$ (i.e., for comparatively short mean residence times in system), and their "shortage" in the oposite case. This fact is documented in Fig. 4. The exponential curves represented in terms of Eq. (*41*) (dash line) and converging Eq. (*32*) to it for low values of β and κ_1 (and therefore high h and b) practically coincide. We assume that the method proposed here makes it possible to explain more suitably the existence of "excess" of small particles than the presumption of dispersion of particle growth rates introduced by Larson et al.[14].

Further it was stated that as far as the ideally stirred system is concerned, it is possible (with negligibly small size of entering particles) to describe the particle size distribution in terms of the same differential equation as in non-flow system which, however, contains, in addition, the additive term directly proportional to the sought function (see Eq. (*30*)).

If we set $w() \equiv 0$ in Eq. (*5*), the term in Eq. (*30*) containing second derivative disappears (i.e., the term characterizing the random changes of particle size). We obtain Eq. (*4*), i.e., the well-known population balance[1,*]. The stochastic differential equation (*5*) then turns into an ordinary differential equation which describes only the change of particle size without action of random effects. For instance, the right-hand side of Eq. (*17*) is then identically equal zero, and the variance of distribution (with zero initial value) then remains zero during the whole further process.

From the above-mentioned follows, that the population balance as a first-order partial differential equation, is unable to describe the random development of particle

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* Weng[26] pointed out the relation between the randomization of time parameter and the solution of population balace in a paper dealing with flow crystallizers.

population in a non-flow system (unless, e.g., we consider the rate of size change or boundary condition as a stochastic function of time), and that the particle size distribution in a flow system is conditioned only by residence time distribution of these particles. For a more detailed description of population development it would be therefore suitable to complete Eq. (*4*) by a "diffusional" term. This fact was pointed out by Randolph and White[19] who recommended such a formal complementing so that the "diffusivity" – as we have already stated – considered as a constant. The approach proposed by us, i.e., use of SDE, this diffusion term directly implies, from the preceding considerations of boundary conditions folloving that this "diffusivity" has to depend on particle size, namely, that its value has to converge to zero (from the right) on diminishing the size to infinitesimal dimension.

CONCLUSIONS

1. The application of stochastic differential equations was proposed to the description of changes of solid particle size during crystallization, polymerization, abrasion and the like; the adequate diffusion equations then make it possible to describe the time development of population of these particles.

2. The particular forms of coefficients in these equations were proposed which lead to the description of time development of populations for the most often used distributions (normal, lognormal, gamma distributions).

3. This approach was employed even for the flow system; the methods of computation of density of particle size distribution were proposed on the basis of knowledge of distribution of particle residence times in this system and simultaneous knowledge of density of their size distribution in non-flow system.

4. It was shown that the population balance in the usually used form (Eq. (*4*)) does not make it possible to simply describe the time development of these populations in

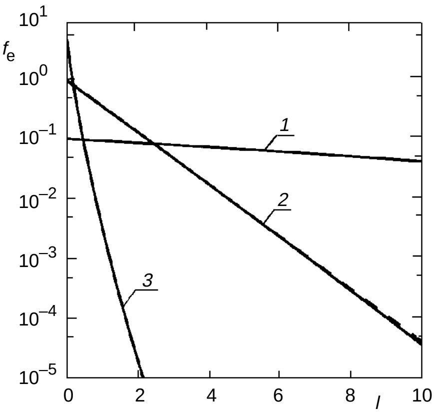

FIG. 4
Density of particle size distribution in flow ideally stirred system. Solid lines *1*–*3* according to Eq. (*32*), dashed line according to Eq. (*41*). Parameters: λ = 1.02, $\bar{t}\alpha = 1/\lambda$; *1* b = 50, h = 5; *2* b = 51, h = 50; *3* b = 5, h = 50

non-flow systems, and therefore its complementing was proposed by the “diffusional” term with “diffusivity” which is a function of particle size.

APPENDIX

Solution of Equation (12) for q = 1/2

All the terms of Eq. (*12*) are divided by parameter β, and new variables $\tau \equiv \beta t$; $z \equiv \lambda l = (2\beta/\kappa_1^2) l$ are inserted:

$$\frac{\partial f_t}{\partial \tau} + \frac{\partial (b - z) f_t}{\partial z} - \frac{\partial^2 z f_t}{\partial z^2} = 0 \qquad [b > 0] \ . \qquad (A1)$$

The stationary solution of this equation (for $\partial f_t / \partial \tau \equiv 0$) is

$$f_s(z) = C z^{b-1} \exp(-z) \ . \qquad (A2)$$

The value of integration constant $C = 1/\Gamma(b)$ is calculated from the condition that function $f_s()$ should be the probability density and its integral in limits from zero to infinity has to equal unity. A general solution of Eq. (*A1*) will be sought in the form

$$f_t = z^{b-1} \exp[-(z - \nu\tau)] \, y(z) \ , \qquad (A3)$$

where ν = const and y is the sought function of variable z. After inserting into Eq. (*A1*) and rearranging we get the relation

$$z \frac{d^2 y}{dz^2} + (b - z) \frac{dy}{dz} - \nu y = 0 \ , \qquad (A4)$$

whose solution is the equation $y = A\Phi(\nu, b; z) + Bz^{1-b}\Phi(\nu - b + 1, 2 - b; z)$, where Φ is the so-called confluent hypergeometric function[27]. Integration constant B has to be equal zero for otherwise the solution would not converge to the stationary solution according to Eq. (*A2*) on growing τ ad infinitum. It is further well-known[28] that for $\nu = n = 0, -1, -2, -3, \ldots$, function $\Phi()$ turns into the generalized Laguerre polynomial $L_n^{(b-1)}(z)$ so that the single partial solutions of Eq. (*A4*) are $y_n(z) = A_n L_n^{(b-1)}(z)$ and further the general solution of Eq. (*A1*)

$$f_t(z;\tau \,|\, z_p) = z^{b-1} \exp(-z) \sum_{n=0}^{\infty} A_n L_n^{(b-1)}(z) \exp(-n\tau) \ . \qquad (A5)$$

Constants A_n are determined from the initial condition; for the transitive probability density has to hold $\lim_{t\to 0} f_t(z;\tau| z_p) = \delta(z - z_p)$. Therefore we multiply both sides by $L_m^{(b-1)}(z)$ and integrate with $\tau = 0$

$$\int_0^{\infty} \delta(z - z_p) L_m^{(b-1)}(z)\, dz = \sum_{n=0}^{\infty} A_n \int_0^{\infty} z^{b-1} \exp(-z) L_n^{(b-1)}(z) L_m^{(b-1)}(z)\, dz \ . \qquad (A6)$$

With regard to the orthogonal properties of the Laguerre polynomials, the value of integral on the right-hand side is equal zero when $m \neq n$, in the opposite case it is equal $\Gamma(b + n)/n!$ (ref.[27]). For the integration constants therefore holds: $A_n = L_n^{(b-1)}(z_p) n!/\Gamma(b + n)$. After inserting these relations into Eq. (*A5*), we finally have the general solution

$$f_t(z;\tau \,|\, z_p) = z^{b-1} \exp(-z) \sum_{n=0}^{\infty} \frac{n!}{\Gamma(b+n)} L_n^{(b-1)}(z_p) L_n^{(b-1)}(z) \exp(-n\tau) \ . \qquad (A7)$$

The expression on the right-hand side can be summed up[28] and after inserting the original variables and rearranging we get the general relation for transitive probability density

$$f_t(l;t \,|\, l_p) = \left[\frac{l}{l_p \Theta}\right]^{(b-1)/2} \exp\left[-\frac{\lambda(l + l_p\Theta)}{1-\Theta}\right] I_{b-1}\left[\frac{2\lambda(l l_p \Theta)^{1/2}}{\Theta}\right] \frac{\lambda}{1-\Theta} \ . \qquad (A8)$$

Symbol I stands for the modified Bessel function. In case that the initial probability density describes the gamma distribution as well in the form $f_p(l_p) = f_G(l_p; g/\bar{l}_p, g)$, where $\bar{l}_p$ is the mean value of initial distribution and parameter $g \neq b$, we obtain after integrating, indicated by Eq. (*7*), the general relation[28]

$$f(l;t) = f_G[l;\lambda/(1-\Theta), g](1 - H)^g \Phi[g,b;\lambda l H/(1-\Theta)] \ , \qquad (A9)$$

where $H \equiv \lambda\bar{l}_p\Theta/[\lambda\bar{l}_p\Theta + g(1-\Theta)]$. In case $g = b$, function Φ is simplified: $\Phi(b,b;x) = \exp(x)$, and Eq. (*A9*) turns into Eq. (*22*).

Feller (cited according to ref.[10]) presents a solution for the particular case when $\alpha = 0$ and consequently $b = 0$. Equation (*A8*) is in addition rather simplified regarding the relation $I_{-1}(x) = I_1(x)$ (ref.[28]). If we insert this Feller solution into the integral in Eq. (*38*) and use the dimensionless variables $u \equiv \lambda l/(1 - \Theta)$ and $u_p \equiv \lambda l_p\Theta/(1 - \Theta)$, we obtain after integrating[28]

$$\int_0^\infty (u/u_p)^{-1/2} \exp[-(u+u_p)] I_1[2(uu_p)^{1/2}]\,\mathrm{d}u = u_p \exp(-u_p)\Phi(1,2;u_p) \quad . \tag{A10}$$

From the definition of confluent hypergeometric function follows that $\Phi(1,2;x) = [\exp(x) - 1]/x$. After rearranging the right-hand side of Eq. (*A10*) with regard to the last relation and backward inserting we get the solution of integral in Eq. (*39*).

Solution of Equation (12) for q = 1 and α = 0

$$\frac{\partial f_t}{\partial t} - \beta \frac{\partial (l f_t)}{\partial l} - \frac{1}{2}\kappa_2^2 \frac{\partial^2 (l^2 f_t)}{\partial l^2} = 0 \quad . \tag{A11}$$

As it is reported by Sveshnikov[22], Eq. (*A11*) is to be solved easily by exchanging variables when we set $x \equiv \log(l) + (\kappa_2^2/2 + \beta)t$ and $\tau \equiv \kappa_2^2 t$. Then we obtain the well-known diffusion equation $\partial f'/\partial\tau - \partial^2 f'/\partial x^2 = 0$, whose fundamental solution[29] $f'(x;\tau|\, x_p) = f_N(x;x_p,\tau)$ is backward inserted into. We get the relation for the transitive probability density

$$f_t(l;t \,|\, l_p) = f_N[\log l;\, \log l_p - (\kappa_2^2/2 + \beta)t, \kappa_2^2 t]/l \quad . \tag{A12}$$

As an initial condition we choose the probability density of lognormal distribution $f_p(l_p) = f_N[\log l_p; \log[\overline{l(0)}/r(0)], \log r^2(0)]/l_p$, where r^2 and $\bar{l}$ are defined behind Eq. (*24*). After inserting from the last two relations into Eq. (*7*) and after integrating, we obtain Eq. (*24*). If we insert into expressions for the two parameters in Eq. (*24*) from the definition relations behind this equation, we get $\log[\overline{l(t)}/r(t)] = \log[\bar{l}_p^2/(\sigma_p^2 + \bar{l}_p^2)^{1/2}] - (\beta + 1/2\kappa_2^2)t$ and $\log[r^2(t)] = \log[\sigma_p^2/\bar{l}_p^2 + 1] + \kappa_2^2 t$, where follow non-equalities (*36*) from.

Recording and Solving the Relations for Flow System

By analogy with the monograph by Carslaw and Jaeger[29], it is possible to prove, by direct substitution, the statement that if we know the solution $g_A(x,t)$ of the partial differential equation

$$\frac{1}{2}\frac{\partial^2[w^2(x) g_A(x,t)]}{\partial x^2} - \frac{\partial[v(x) g_A(x,t)]}{\partial x} - A g_A(x,t) - \frac{\partial g_A(x,t)}{\partial t} = 0 \tag{A13}$$

for $A = 0$, then the solution $g_A(x,t)$ for $A \neq 0$ can be found by means of the relation

$$g_A(x,t) = A\int_0^t \exp(-As)g_0(x,s)\,\mathrm{d}s + g_0(x,t)\exp(-At) \qquad [g_0(x,0) = 0] \ . \qquad (A14)$$

For $A > 0$ and $t \rightarrow \infty$, the last term on the right-hand side of the equation disappears, which proves the identity between the solution of Eq. (*30*) and of integral (*9*) for $f_f = A \exp(-At)$ $[A = 1/\overline{t}]$ and $t \rightarrow \infty$. The condition of validity written in square brackets behind Eq. (*A14*), however, sets a limit to this statement just to the case of negligible value of initial particle sizes. When solving Eq. (*31*), we proceed by analogy with the solution of Eq. (*A1*); we get Eq. (*A4*), where $\nu = 1/\overline{t}$. Its solution is an expression which contains a confluent hypergeometric function, however, this time in the form proposed by Tricomi[27]

$$f_e(l) = h\Gamma(h)f_G(l;b/\overline{l}_s,b)\Psi[h,b;(bl/\overline{l}_s)] \ , \qquad (A15)$$

where function Ψ is defined in List of Functions, $\overline{l}_s \equiv \alpha/\beta$, $b \equiv 2\alpha/\kappa_1^2$ and $h \equiv 1/(\beta\overline{t})$. Equation (*A15*) is further rearranged so that the function $f_G()$ is written under the symbol of integral in function Ψ, and the integration variable changed. So we obtain the integral in Eq. (*32*).

From the definition of the gamma function follows that for every $h = b - 1$, relation (*32*) changes to exponental function $f_e(l) = \lambda \exp(-\lambda l)$. On converging the parameters β and κ_1 to zero, $(1/\beta\overline{t}) \approx (2\alpha/\kappa_1^2)$ where the relation $(1/\alpha\overline{t}) \approx (2\beta/\kappa_1^2) = \lambda$ follows from, which proves the statement before Eq. (*41*). It further follows from the definition of the gamma function that the value of integral for negligibly small particle size is equal

$$f_e(0) = \lambda h\Gamma(b-1)/\Gamma(b) = \lambda h/(b-1) \ . \qquad (A16)$$

Inasmuch as the value of integral from function $f_e(l)$ over the entire range of variable l equals unity, it proves the statement given behind Eq. (*41*).

LIST OF FUNCTIONS

Probability density of normal distribution:

$$f_N(x;\overline{x},\sigma^2) \equiv \frac{1}{\sqrt{2\pi\sigma^2}}\exp\left[-\frac{(x-\overline{x})^2}{2\sigma^2}\right] \ . \qquad (a)$$

Probability density of gamma distribution:

$$f_G(x;g,h) \equiv \frac{g}{\Gamma(h)}(gx)^{h-1} \exp(-gx) \quad . \tag{b}$$

Modified Bessel function:

$$I_p(x) \equiv \sum_{k=0}^{\infty} \frac{(x/2)^{2k+p}}{k!\,\Gamma(k+p+1)} \quad . \tag{c}$$

Generalized Laguerre polynomial:

$$L_n^{(b-1)}(z) \equiv \Gamma(n+b) \sum_{k=0}^{n} \frac{(-z)^k}{\Gamma(k+b)k!\,(n-k)!} \quad . \tag{d}$$

Gamma function:

$$\Gamma(b) \equiv \int_0^{\infty} x^{b-1} \exp(-x)\,\mathrm{d}x \quad . \tag{e}$$

Confluent hypergeometric function:

$$\Phi(a,b;x) \equiv \sum_{n=0}^{\infty} \frac{\Gamma(a+n)\,\Gamma(b)x^n}{\Gamma(a)\,\Gamma(b+n)n!} \quad . \tag{f}$$

Confluent hypergeometric function (by Tricomi[27]):

$$\Psi(c,b;x) \equiv \frac{1}{\Gamma(c)} \int_0^{\infty} \exp(-xs)s^{c-1}(1+s)^{b-c-1}\,\mathrm{d}s \qquad [x > 0,\, c > 0] \quad . \tag{g}$$

LIST OF SYMBOLS

a	parameter of gamma distribution with reciprocal argument in Eq. (*23*) [$a \equiv 2\beta/\kappa_2^2$]
b	parameter of gamma distribution in Eq. (*22*) [$b \equiv 2\alpha/\kappa_1^2$]
c	parameter of gamma distribution of residence times in Eq. (*26*)
F	distribution function
f	probability density (of particle size distribution), L^{-1}
G	stochastic quantity with normal distribution
h	parameter in Eq. (*32*) [$h \equiv 1/\beta\overline{t}$]
$L(t)$	characteristic dimension (size) of particle (stochastic time function), L
l	particle size (variable of distribution), L
N	number of particles

n	density of particle population, L^{-4}
P	parameter in Eq. (*35*), T^{-1}
p	portion of particles of "negative" size
Q	parameter in Eq. (*35*), $T^{-1/2}$
q	parameter characterizing particle size distribution
r	parameter of lognormal distribution in Eq. (*24*)
t	time, T
V	suspension volume in system, L^3
v	rate of change of particle size, $L\ T^{-1}$
$W(t)$	Wiener process, $T^{1/2}$
w	random rate contribution, $L\ T^{-1/2}$
α	constant rate of particle growth, $L\ T^{-1}$
β	coefficient characterizing rate of change of particle size, T^{-1}
γ	exponent in Rosin–Rammler distribution
ε	parameter in Eq. (*37*) [$\varepsilon \equiv \gamma - 1$]
Θ	time factor in Eq. (*14*) [$\Theta \equiv \exp(-\beta t)$]
κ_{2q}	coefficient characterizing random rate of change of particle size, $L^{1-q}\ T^{-1/2}$
λ	scaling parameter of gamma distribution in Eq. (*32*) [$\lambda \equiv 2\beta/\kappa_1^2$], L^{-1}
σ_{2q}^2	variance of particle size, L^2

Indexes and other signs

e	referred to outlet stream
f	referred to flow system
G	referred to gamma distribution
N	referred to normal distribution
p	referred to beginning of process
s	referred to stationary state
T	referred to whole system
t	referred to transitive probability density
*	referred to empirical distribution
$\bar{u}$	mean value of quantity u

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