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Elliptic random-walk equation for suspension and tracer transport in porous media

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ABSTRACT

We propose a new approach to transport of the suspensions and tracers in porous media. The approach is based on a modified version of the continuous time random walk (CTRW) theory. In the framework of this theory we derive an elliptic transport equation. The new equation contains the time and the mixed dispersion terms expressing the dispersion of the particle time steps. The properties of the new equation are studied and the fundamental analytical solutions are obtained. The solution of the pulse injection problem describing a common tracer injection experiment is studied in greater detail. The new theory predicts delay of the maximum of the tracer, compared to the velocity of the flow, while its forward "tail" contains much more particles than in the solution of the classical parabolic (advection-dispersion) equation. This is in agreement with the experimental observations and predictions of the CTRW theory.

1. Introduction

Suspension and tracer flows in porous media appear in a large number of practically important processes and applications: in petroleum engineering [1,2], hydrology and geophysics [3], chemical engineering [4,5], environmental studies [6,7]. Importance of the subject has resulted in multiple studies, both experimental and theoretical [8,9], as well as generalization and analysis of the natural observations and large-scale experiments [10,11].

The described processes are rather complex. They are affected by a number of random factors, like inherent multiscale heterogeneity of the porous medium, particle and pore size distributions, different capture mechanisms (for the suspension flows). However (or, probably, exactly because of this complexity) the classical description of the transport is relatively simple. Usually, the advection-dispersion (AD) equation is applied [9], with a capturing term added for the suspensions [12, 13]. Additional equations describing the effects of captured particles on the parameters of the porous medium (porosity, permeability…) may be involved for the concentrated suspensions [14]. In the cases of the polydisperse suspensions it is also important to consider the particle and the pore size distributions [14]. These distributions are not considered in the present work. In order to present the basic ideas of our derivation in the simplest possible way, we restrict ourselves with the simplest case of a monodisperse low-concentrated suspension or of a tracer. Further generalizations will be subject to a separate work.

Experimental studies of flows in stochastically heterogeneous media referred to above indicate discrepancies between the experimental and the AD-based theoretical predictions. Initially these discrepancies were attributed to the multiple-scale heterogeneities and discussed in the literature as a "scale problem" [9,15]. However, later it was shown experimentally that the discrepancies appear even in the "quasi-homogenous", stochastically-heterogeneous media, if the scale of

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heterogeneity is much smaller than the scale of the problem [9,16]. The experiments, both laboratory and large-scale, are often carried out by the pulse injection of the tracer or of the suspension. It has been observed that (contrary to prediction of the AD theory) the maximum of concentration moves slower than the average velocity of the flow. Meanwhile, the first significant portion of the tracer arrives much faster, and, correspondingly, breakthrough occurs faster than expected [16]. Similar effects were observed under continuous injection of suspensions [17,18].

It was suggested applying a variable time-dependent dispersion coefficient in order to describe such a behavior [15]. This approach is not convenient, however, since it is difficult to evaluate the time variation of the apparent dispersion coefficient for the different geometries of the flow.

A recent approach to modeling the transport in porous media is based on the application of the continuous time random walks (CTRW). The fundamentals of the theory are described in Ref. [19], and review of the recent applications in geophysics in [3]. The essence of this approach is in description of the ensemble of the particles, which jump randomly and independently of each other between the different positions, spending a random time in each of them. Extensive comparison with numerous laboratory and large-scale experiments [3,20] has shown that this approach is capable of the adequate description of the observed concentration profiles, and is significantly more precise that the AD theory.

A disadvantage of the CTRW approach is in the complexity of the obtained integral–differential transport equations. These equations are difficult to solve, analytically or numerically, for a large variety of the initial and boundary conditions, which may arise in practically important problems. Moreover, the non-local boundary conditions may be non-trivial, especially, for multidimensional problems. Another disadvantage is a necessity for the expression for the stochastic kernel depending on time and spatial variables [21,22]. It was shown [3,20] that the only asymptotic form of this kernel is important for the description of the experimental observations. However such a multidimensional asymptotics may be rather non-trivial.

The CTRW approach may be interpreted as a "stochastic discretization" of the random continuous motion of the particles. For the case of pure diffusive process, with no convection or capturing, it was shown that, in the limit of the infinitely small steps, an integral–differential equation describing such motion is reduced to the elliptic differential equation [23]. Unlike the classical Fick–Einstein diffusion equation, a new equation contains an additional term proportional to the second time derivative of the concentration. This term, $D_t\partial^2 c/\partial t^2$, describes dispersion of the randomly walking particles in time, similarly to diffusive term $D_x\partial^2 c/\partial x^2$ describing dispersion of the particles in space. Analytical solutions of the newly derived equation were obtained. It was shown that, compared to the traditional diffusion equation, the new equation predicts that more particles will delay at the origin and, simultaneously, more particles will move far away from it.

The goal of the present paper is to extend the approach developed in Ref. [23] onto the problem of convective-dispersive motion with capturing characteristic of the tracer or dilute suspension motion in porous media. We derive the corresponding transport equation, generalizing the equation obtained in Ref. [23]; study its basic properties; suggest some ideas for evaluation of the transport coefficients; obtain the fundamental solutions; study their properties and compare them qualitatively with the previously obtained CTRW solutions and experimental observations. We show that the new theory is really capable of explaining the qualitative experimental observations. This is shown on the basis of the analytical solution of the pulse injection problem derived in the paper.

The paper is organized as follows. Section 2 introduces a Master equation describing tracer or suspension transport in a porous medium. This equation is derived in a "naïve" or "physical" way; a rigorous mathematical derivation is presented in Appendices A–C. We study basic properties of the derived equation and of its coefficients, and possible simplifications for the different model cases. Section 3 presents solutions of the two problems: the Riemann problem and the problem of pulse injection. These problems are not only important mathematically, but also describe typical laboratory experiments on suspension or tracer flow. Section 4 presents sample calculations showing dependence of the obtained solution on the different coefficients in the equation and comparing it qualitatively with the experimental observations. Finally, the main conclusions are presented.

2. Master equation for suspension flow in porous media

2.1. Derivation of the equation

Historically the first stochastic approach to derivation of a transport equation was developed by Einstein [24] in his theory of Brownian motion. According to the modern source [25], Einstein's derivation contains most of the physical concepts behind the theory of continuous random motion. The Einstein derivation is straightforward and transparent. Therefore, it is worth considering his approach as a starting point, and then to extend it onto our case. A more rigorous derivation may be carried out following Refs. [19,23]. We present this derivation in Appendices A–C.

Einstein considers one-dimensional diffusion as random motion of the particles, which make independent steps (jumps) in fixed time intervals τ. If $f(l)$ is a distribution of one step, then the master transport equation for number particle concentration $c(x, t)$ has the form of

$$c(x, t+\tau) = \int c(x-l, t) f(l)\mathrm{d}l. \tag{1}$$

This equation states, simply, that all the particles that have been at points $x - l$ at the moment t gather at point x at the moment $t + \tau$ with the probability $f(l)\mathrm{d}l$. For our goals it is convenient to rewrite Einstein's equation in the equivalent

form

$$c(x,t) = \int c(x-l, t-\tau) f(l) \mathrm{d}l. \tag{2}$$

For the free (molecular) diffusion it is natural to assume that distribution $f(l)$ is symmetric:

$$f(l) = f(-l). \tag{3}$$

Einstein expands c in both sides of Eq. (1) up to the first non-disappearing terms: second-order in x and first-order in τ. As a result of averaging, he obtains the classical diffusion equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial t^2}, \qquad D = \frac{\langle l^2 \rangle}{2\tau}, \qquad \langle l^2 \rangle = \int l^2 f(l) \mathrm{d}l. \tag{4}$$

It should be noted that Eqs. (1) and (2), while equivalent when expanded up to first-order terms, become non-equivalent when expanded further. Such expansion may possess a physical meaning, as shown in Ref. [23], and will be discussed later for a more general case.

The first generalization comes from the fact that in the porous medium times τ may be distributed along with distances l. The porous medium may be visualized, with some degree of approximation, as a complex graph where two fixed points may be connected by many different pathways. The particles of a tracer or of a suspension move in the porous medium both in "Brownian" and "dispersive" way, the second being determined by the random velocity field of the carrying fluid. This results in the two modifications of Eq. (2) (which, for our goals, is more convenient than (1), as mentioned before). First, not only traveling distances, but also traveling times become distributed, and their distribution may depend on the distribution of the traveling distances. Hence, instead of $f(l)$ it is necessary to introduce the mutual distribution $f(l, \tau)$. Second, assumption (3) is not further valid (except for special cases), hence, first-order terms are retained in the expansion. The integral master equation for this case assumes the form

$$c(x,t) = \int c(x-l, t-\tau) f(l, \tau) \mathrm{d}l \mathrm{d}\tau. \tag{5}$$

Representing integrand $c(x-l, t-\tau)$ in Taylor's series for small l and τ and keeping terms up to second order, we obtain

$$c\,(x-l, t-\tau) = c\,(x,t) - l\frac{\partial c}{\partial x} - \tau\frac{\partial c}{\partial t} - \frac{l^2}{2}\frac{\partial^2 c}{\partial x^2} - \frac{\tau^2}{2}\frac{\partial^2 c}{\partial t^2} - l\tau\frac{\partial^2 c}{\partial x \partial t}.$$

Substitution of this expansion into Eq. (5) results in the second-order partial differential equation generalizing Eq. (4):

$$\langle \tau \rangle \frac{\partial c}{\partial t} + \langle l \rangle \frac{\partial c}{\partial x} = \frac{\langle l^2 \rangle}{2}\frac{\partial^2 c}{\partial x^2} + \frac{\langle \tau^2 \rangle}{2}\frac{\partial^2 c}{\partial t^2} + \langle l\tau \rangle \frac{\partial^2 c}{\partial x \partial t}. \tag{6}$$

Here and further we denote

$$\langle l^n \tau^m \rangle = \int l^n \tau^m f(l, \tau) \mathrm{d}l \mathrm{d}\tau. \tag{7}$$

Further generalization comes from inclusion of the physical mechanism of capturing the particles in the pores, so that they are lost from the flow. The particles can be captured by the different physical mechanisms: adsorption, size exclusion, attachment, diffusion, gravity separation etc. [13]. The capturing mechanisms strongly depend on the sizes and compositions of the particles and of the porous medium, and will certainly be different for tracers and suspensions. Therefore, probabilities of particle capture may be very different. They may also depend on the micro- and mesoscale heterogeneity of the porous medium. In the model considered, this may be taken into account by relating the probabilities of capturing with the lengths and the travelling times of the particles. We introduce mutual distribution $f(l, \tau, p)$ of lengths, times and of the probabilities p to be NOT captured. The integral master equation assumes the form of

$$c(x,t) = \int pc(x-l, t-\tau) f(l, \tau, p) \mathrm{d}l \mathrm{d}\tau \mathrm{d}p. \tag{8}$$

Although straightforward expansion, similar to the above, is possible, it is more convenient to expand Eq. (8) in a different way. Introduce the overall probability P for a particle to pass through a pore

$$P = \int pf(l, \tau, p) \mathrm{d}l \mathrm{d}\tau \mathrm{d}p.$$

Eq. (8) may be rewritten in the form of

$$c(x,t) = P \int c(x-l, t-\tau) s(l, \tau) \mathrm{d}l \mathrm{d}\tau. \tag{9}$$

Here $s(l,\tau)$ is the flight distribution for the particles that remain in the flow:

$$s(l,\tau)=\frac{1}{P}\int pf(l,\tau,p)\mathrm{d}p. \tag{10}$$

Similarly to Eq. (7), we will denote

$$\left\langle l^n\tau^m\right\rangle_p=\int l^n\tau^m s(l,\tau)\mathrm{d}l\mathrm{d}\tau. \tag{11}$$

Then $\langle 1\rangle_p=1$, and expansion similar to (6), after division by $P\langle\tau\rangle_p$, assumes the form

$$\frac{\partial c}{\partial t}+v\frac{\partial c}{\partial x}=D_x\frac{\partial^2 c}{\partial x^2}+D_t\frac{\partial^2 c}{\partial t^2}+D_{xt}\frac{\partial^2 c}{\partial x\partial t}-\Lambda c. \tag{12}$$

Here v is interstitial (hydrodynamic) velocity of a particle, Λ is the filtration coefficient per unit time, D_x, D_t and D_{xt} are the spatial, temporal and mixed dispersion coefficients, correspondingly:

$$v=\frac{\langle l\rangle_p}{\langle\tau\rangle_p},\qquad D_x=\frac{\left\langle l^2\right\rangle_p}{2\langle\tau\rangle_p},\qquad D_t=\frac{\left\langle\tau^2\right\rangle_p}{2\langle\tau\rangle_p},\qquad D_{xt}=\frac{\langle l\tau\rangle_p}{\langle\tau\rangle_p},\qquad \Lambda=\frac{1-P}{P\langle\tau\rangle_p}. \tag{13}$$

The terms on the left-hand side of Eq. (12) describe convective motion of the suspension. The terms on the right-hand side represent dispersion/diffusion, as well as particle capture rate Λc, where Λ is filtration coefficient.

Eqs. (8) and (12) describe motion of the suspension in one dimension, or projection of such a motion on a given axis. Generalization onto multidimensional flows is straightforward and will not be considered here.

The previous derivation of both integral and differential master equations is by no means strict. An obvious shortcoming of the derivation is absence of the explanation why the expansion to the second order is better than any other (let us say, to the first or to the third order). The original logic of Einstein was to retain first non-disappearing terms. However, this logic, perfectly working for the case of the "pure" diffusion, where condition (3) is valid, fails to reproduce the traditional equation for convective diffusion-dispersion. In this case it would result in only the first-order convective term remaining, while the second-order dispersion terms would disappear. On the other hand, "blind" keeping all the second-order terms leads to the complete equation (12) containing non-traditional second-order time and mixed derivatives.

An answer about the choice of a proper differential equation is found on the following way. An integral master equation, such as (8), represents evolution of the particles in the course of a single random step. The considered transport process is a superposition of multiple small steps. Ideally, a limit of an infinite number of infinitely small steps in time and space should be considered. In such a limit, motion of a particle becomes a random process with continuous trajectories. A partial differential equation, like (8), should describe evolution of the concentration of the particles undergoing this limiting process.

In this sense, Eq. (13) should be understood asymptotically, in the limit of small values of $\langle\tau\rangle_p$ and $\langle l\rangle_p$:

$$\begin{aligned} &v=\lim_{\langle\tau\rangle_p\to 0}\frac{\langle l\rangle_p}{\langle\tau\rangle_p},\qquad D_x=\lim_{\langle\tau\rangle_p\to 0}\frac{\left\langle l^2\right\rangle_p}{2\langle\tau\rangle_p},\qquad D_t=\lim_{\langle\tau\rangle_p\to 0}\frac{\left\langle\tau^2\right\rangle_p}{2\langle\tau\rangle_p},\\ &D_{xt}=\lim_{\langle\tau\rangle_p\to 0}\frac{\langle l\tau\rangle_p}{\langle\tau\rangle_p},\qquad \Lambda=\lim_{\langle\tau\rangle_p\to 0}\frac{1-P}{\langle\tau\rangle_p}. \end{aligned} \tag{14}$$

In order to retain all the terms in the equation, values of $\langle l\rangle_p$, $\left\langle l^2\right\rangle_p$, $\left\langle\tau^2\right\rangle_p$, $\langle l\tau\rangle_p$, $1-P$ should be of the same order of magnitude as $\langle\tau\rangle_p$. Since second moments of the distributions (like Gaussian or log-normal) are independent of the first moments, this requirement is non-contradictory. Thus, a program for proof of Eq. (12) is: to consider a CTRW process with finite first and second moments of one step; to consider a limit where this step tends to zero; and, assuming that the trajectories of the particles in such a limit become continuous, prove that such a limiting process obeys Eq. (12). Finiteness of the first and the second moments is a necessary requirement. An opposite case, anomalous diffusion [20], is not considered here.

The program described above is carried out in Appendices A and B. Appendix C shows that expression Λc really describes the capture term for the process considered.

It should also be noted that in the limit of the infinitely small steps probability P for a particle to be not captured during one flight should tend to unity, otherwise all the particles would be captured at very beginning. This also follows from the last Eq. (14). Since $0\le p\le 1$, tendency $P\to 1$ is only possible if the distribution of p tends to be concentrated at unity: $f(p)\to\delta(p-1)$. However, the difference between the two methods of averaging: $\langle\rangle_p$ and $\langle\rangle$ for the different moments $l^n\tau^m$ does not disappear in this limit. While $\langle\rangle$ is the average over all the particles, $\langle\rangle_p$ is the average only over the particles that are not captured. In order to simplify the designations, in the following we omit subscript p in $\langle\rangle_p$ and use only this average, unless specified.

The last comment to the derivation is that the value of v reflects the average hydrodynamic, interstitial velocity of the flow [26]. In order to express Eq. (12) in terms of the superficial velocity (flow rate per unit area), it should be multiplied by porosity ϕ.

2.2. Examples

Important particular cases arise from particular choices of distribution $f(l, \tau, p)$ or from assumptions about its structure. A possible simplifying assumption is that the probability for a particle to be captured is a function of the length of the flight:

$$p = p(l). \tag{15}$$

In this case function $f(l, \tau, p)$ assumes the form of

$$f = f_0(l, \tau)\delta(p - p(l)). \tag{16}$$

Correspondingly, the expressions for the transport coefficients may be simplified: for example,

$$P = \int p(l) f_0(l, \tau) \mathrm{d}l\mathrm{d}\tau.$$

For short particle flights, it may be assumed that the passing probability is proportional to path:

$$p = 1 - \lambda_m |l|. \tag{17}$$

The microscopic filtration coefficient λ_m is, generally speaking, different from the macroscopic coefficient Λ introduced in Eq. (14). For the case where all the flights are positive, it is easy to prove that $\Lambda = \lambda_m v$. For larger l Eq. (17) may produce negative values of p. In this case it is reasonable to consider exponential dependence for $p(l)$:

$$p = \mathrm{e}^{-\lambda_m |l|}.$$

Such dependence may be derived, for example, by assuming that the pores (particle paths) are uniform and, thus, the particle may be captured at each infinitesimal cut of the flight with equal probability, independent on the pre-history of the flight. This is a standard starting assumption in the derivation of the exponential distribution [27].

An assumption alternative to (16) is that distance l may be passed by the different pathways, and each pathway corresponds to a different passing probability. Assume, as a simplest example, that a particle may move between the two neighboring points by the two alternative paths. Each path is selected with equal probability of 1/2. The flight times along these paths are τ_1 and τ_2, and the passing probabilities are p_1, p_2, correspondingly. Then distribution $f(l, \tau, p)$ assumes the form of

$$f(l, \tau, p) = f(l)\left[\frac{1}{2}\delta(\tau - \tau_1)\delta(p - p_1) + \frac{1}{2}\delta(\tau - \tau_2)\delta(p - p_2)\right].$$

This model allows for further generalizations.

Let us now consider special distributions with regard to l and τ. If convection is absent, it is reasonable to assume that the particle displacements forward and backward are equiprobable:

$$f(l, \tau, p) = f(-l, \tau, p). \tag{18}$$

In case of (16) it is reasonable to additionally assume that $p(l) = p(-l)$. Then $\langle l \rangle = 0$, $\langle l\tau \rangle = 0$, and, according to Eq. (13), both convective and mixed diffusive terms in transport Eq. (12) disappear. This equation is reduced to the elliptic diffusion equation [23] with the additional capture term:

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} + D_t \frac{\partial^2 c}{\partial t^2} - \Lambda c.$$

Another case where mixed diffusive term disappears is where l and τ are distributed independently: $s(l, \tau) = s(l)s(\tau)$. In this case, according to Eq. (13), $D_{xt} = \langle l \rangle$, that is, it disappears as the flight distance tends to zero.

An important case of the vanishing diffusion is where either length or the time of flight is fixed. Assume for example that all the lengths of the flight are equal, or, the same, $f(l) = \delta(l - l_0)$. Then $D_x = l_0^2 / \langle \tau \rangle$, and $D_{xt} = l_0$. In order to keep velocity finite in the limit of infinitely small steps, l_0 should tend to zero, at least, as fast as $\langle \tau \rangle$. Therefore, both D_x and D_{xt} in this limit disappear. However, the time dispersion coefficient D_t may remain finite. Similarly, if τ is fixed to τ_0, both D_t and D_{xt} vanish, and the transport equation is reduced to the ordinary convection-diffusion (or advection-dispersion) equation, similarly to Einstein's derivation.

2.3. Basic properties

The following Cauchy–Bunyakovsky inequality holds for the second moments:

$$\langle l\tau \rangle^2 \leq \langle l^2 \rangle \langle \tau^2 \rangle. \tag{19}$$

From this inequality it follows that the quadratic form determined by the coefficients D_x, D_{xt}, D_t is always non-negative definite. *Therefore transport* equation (12) *is always elliptic or parabolic.*

Degeneration to a parabolic equation is possible if one of the coefficients D_x, D_t becomes zero. Then it follows from Eq. (19) that the mixed coefficient D_{xt} is also zero. In particular, this happens, if either lengths or times of the flight are fixed, as discussed in the previous subsection.

Let us now discuss the properties of the equation with regard to the Galilean coordinate transformation:

$$X = x - Vt, \quad T = t. \tag{20}$$

The described process is not invariant with regard to this transformation, since the there is a fixed system of coordinates connected to the porous medium. Application of transformation (20) to Eq. (12) results in

$$\frac{\partial c}{\partial T} + (v - V)\frac{\partial c}{\partial X} = D_X \frac{\partial^2 c}{\partial X^2} + D_T \frac{\partial^2 c}{\partial T^2} + D_{XT} \frac{\partial^2 c}{\partial X \partial T} - \Lambda c, \tag{21}$$

$$D_X = D_x - VD_{xt} + D_t V^2, \qquad D_{XT} = D_{xt} - 2VD_t, \qquad D_T = D_t. \tag{22}$$

Unlike the case of "normal" diffusion, the diffusion coefficients in the elliptic case vary under the Galilean transformation. Only coefficient D_t remains unchanged.

As usual, transformation with $V = v$ eliminates the convective term. It may be hoped that such a transformation will also remove the mixed dispersion term $D_{XT}\partial^2 c/\partial X \partial T$. Indeed, assume that in the system of coordinates related to the convective velocity v the particles undergo purely diffusive motion. Then the flight distribution in these coordinates becomes symmetric (see Eq. (18)), and both convective and mixed diffusive terms disappear. The formulated assumption looks valid for the case of a purely molecular diffusion (the motion of a particle consists of a convective displacement plus a purely diffusive jump). However, it is not certain for the case of convective dispersion. In any case, the condition for disappearance of the mixed diffusive term has the form of

$$D_{xt} - 2vD_t = 0, \quad \text{or} \quad \frac{\langle l \rangle}{\langle \tau \rangle} = \frac{\langle l\tau \rangle}{\langle \tau^2 \rangle}.$$

In the future, we do not necessarily assume that this condition is fulfilled.

2.4. Evaluation of the transport coefficients in porous media

Let us consider the case where convective flux is non-zero and convective dispersion is also present in the system. As estimates and experimental data show [26,28], characteristic values of the molecular diffusion coefficients in macroporous media are of the order of magnitude of 10^{-10} to 10^{-11} m^2/s, while the dispersion coefficients are normally several orders of magnitude higher. Hence, convective dispersion may often be considered as a dominating mechanism of the Fickean mass transfer.

Based on Eq. (13), let us transform the expressions for some transport coefficients to the following form:

$$D_x = \alpha_D v, \qquad \Lambda = \lambda v. \tag{23}$$

Here (omitting limits)

$$\alpha_D = \frac{\langle l^2 \rangle}{\langle l \rangle}, \qquad \lambda = \frac{1 - P}{\langle l \rangle}. \tag{24}$$

Expression (23) for D_x assumes the common form of the expression for the coefficient of convective dispersion. This coefficient is proportional to velocity, the proportionality coefficient being a characteristic diffusive length α_D [26]. As follows from Eq. (24), the diffusive length is a geometrical factor expressing dispersion of the travel lengths in porous media.

The value of λ is the standard filtration coefficient: probability of a particle to be captured per unit of the particle trajectory length. As discussed in Section 2.2, it may coincide with or differ from the microscopic capture coefficient λ_m. Coefficient λ is usually assumed to depend only on the properties of the suspension and of the porous medium, but not on the filtration rate. This is in correspondence with its geometric definition (24).

Both other dispersion coefficients, D_{xt} and D_t, are rate dependent. For their evaluation the common distribution $f(l, \tau)$ (or $s(l, \tau)$) should be determined.

Let us provide an outline for such determination. Assume that the mutual distribution $h(l, r)$ of the pores (or, generally, pathways in a porous medium) by lengths l and hydrodynamic radii r is known. In order to simplify the derivation without loss of physical meaning, assume that flow along each path occurs under the action of the same pressure gradient $|\nabla P|$. Then the average flow velocity u is given by the Poiseuille law

$$u = \frac{r^2}{8\mu}|\nabla P|.$$

By application of the common transformations, it may be found that the flow velocity distribution on microlevel $g(l, u)$ is given by

$$g(l, u) = \sqrt{\frac{2\mu}{|\nabla P| u}}\, h\left(l, \sqrt{\frac{8\mu u}{|\nabla P|}}\right).$$

Since $u = l/\tau$, recalculation of the density distribution from velocities to times gives

$$f(l,\tau) = \frac{l}{\tau^2}\sqrt{\frac{2\mu l}{|\nabla P|\tau^3}}h\left(l, \sqrt{\frac{8\mu l}{|\nabla P|\tau}}\right).$$

Of course, this scheme is oversimplified. More precise results with distributed pressure differences over pores may be obtained by application of the percolation theory [29]. It is not within the scope of this work to discuss them.

2.5. Equation for the deposition rate

The stochastic method of derivation of the master equation, which is explored in the present work, is different from the common mechanical–physical way, where the different terms in the governing equation are introduced on the basis of their physical meaning. Physical interpretation of the different addenda in master equation (12) requires additional derivations.

An important question discussed in the literature is about the shape of the capture term. Classical works [12,13] suggest the transport equation in the form of the flow with first-order chemical reaction (deposition). Within a slight generalization, this system has a form of

$$\begin{aligned} &\frac{\partial c}{\partial t} + \frac{\partial j}{\partial x} = -\frac{\partial \sigma}{\partial t}, \\ &\frac{\partial \sigma}{\partial t} = \lambda v c. \end{aligned} \tag{45}$$

Here j is the particle flux, and σ is the number of the deposited particles, so that $R = \partial\sigma/\partial t$ is the deposition rate. One may either consider only convective flux: $j = vc$, or add the dispersive flux: $j = vc - D\partial c/\partial x$. Then the question arises [31] whether the diffusive correction should also be included into the deposition rate, and the last term of Eq. (45) should read

$$\frac{\partial \sigma}{\partial t} = \lambda \left| vc - D\frac{\partial c}{\partial x} \right|. \tag{46}$$

Eq. (46) means that a particle is captured by a vacancy independently of, whether it is advective or diffusive/dispersive flux that brings the particle to the vacancy. On the microscopic level, however, the directed advective flux plays a different rule than chaotic dispersive motion. Whether these two types of fluxes should enter the capture equation in the same or in different ways, remains an open question.

We show in Appendix C, on the basis of the stochastic arguments, that within our description of the problem, and within the method of averaging (11) used throughout this paper, the capture (deposition) term is equal to Λc.

In order to demonstrate non-triviality of this statement, let us consider the following example considered in Section 2.2. Assume that all the values of l are positive and small, and that the probability of passing a pore may be approximated by $p = 1 - \lambda l$, $0 < l \ll 1$ (see Eq. (17)). Then

$$f(l,\tau,p) = f(l,\tau)\delta(p - (1-\lambda l)).$$

Its substitution into Eq. (8) results in

$$c(x,t) = \int (1-\lambda l)c(x-l, t-\tau)f(l,\tau)\mathrm{d}l\mathrm{d}\tau.$$

Let us remember now the difference between the two averaging procedures suggested in Section 2, and instead of averaging $\langle\rangle_p$ described by Eqs. (8)–(13) apply directly the procedure of expansion and averaging. Retention of the second-order terms results in the following equation:

$$(\langle\tau\rangle - \lambda\langle l\tau\rangle)\frac{\partial c}{\partial t} + \left(\langle l\rangle - \lambda\left\langle l^2\right\rangle\right)\frac{\partial c}{\partial x} = \frac{\left\langle l^2\right\rangle}{2}\frac{\partial^2 c}{\partial x^2} + \frac{\left\langle \tau^2\right\rangle}{2}\frac{\partial^2 c}{\partial t^2} + \langle l\tau\rangle\frac{\partial^2 c}{\partial x \partial t} - \lambda\langle l\rangle c,$$

or

$$\frac{\partial c}{\partial t} + \frac{\langle l\rangle}{\langle\tau\rangle}\frac{\partial c}{\partial x} = \frac{\left\langle l^2\right\rangle}{2\langle\tau\rangle}\frac{\partial^2 c}{\partial x^2} + \frac{\left\langle\tau^2\right\rangle}{2\langle\tau\rangle}\frac{\partial^2 c}{\partial t^2} + \frac{\langle l\tau\rangle}{\langle\tau\rangle}\frac{\partial^2 c}{\partial x\partial t} - \lambda\left(\frac{\langle l\rangle}{\langle\tau\rangle}c - \frac{\langle l\tau\rangle}{\langle\tau\rangle}\frac{\partial c}{\partial t} - \frac{\left\langle l^2\right\rangle}{2\langle\tau\rangle}\frac{\partial c}{\partial x}\right).$$

The term proportional to λ might be interpreted as a capture term containing diffusion-like addendum. However, this is a misinterpretation. Instead, the coefficients like $\langle\tau\rangle - \lambda\langle l\tau\rangle$, $\langle l\rangle - \lambda\left\langle l^2\right\rangle$ should be interpreted as actual decrease of the flight times and lengths due to the fact that some particles become captured. Correspondingly, the flow velocity should be calculated as $v = \left(\langle l\rangle - \lambda\left\langle l^2\right\rangle\right)/(\langle\tau\rangle - \lambda\langle l\tau\rangle) = \langle l\rangle_p/\langle\tau\rangle_p$ etc. It should also be remarked that such "diffusion-like" form of the additional terms arises only if the passage probability is equal to $1 - \lambda l$. Any other expression for the probability would lead to more complicated dependencies, if average $\langle\rangle$ is applied. However, they result in the same differential transport equation when transferring to average $\langle\rangle_p$.

3. Solutions of the specific problems

3.1. Statement of the problems

As mentioned in the Introduction, the process of suspension filtration in a porous medium has commonly been described by the advection-dispersion equation with entrapment [13]. Partial differential equation (12) describing the process of particle filtration in porous media differs from the classical equation by the two terms of the temporal and mixed dispersion: $D_t\partial^2 c/\partial t^2$, $D_{xt}\partial^2 c/\partial x\partial t$. In order to discuss the effect of these terms, we will first consider the classical Riemann problem on the full axis $-\infty < x < \infty$, with the following initial condition:

$$t = 0\text{: } c(x, 0) = 1, \quad x < 0; \qquad c(x, 0) = 0, \quad x > 0. \tag{25}$$

This is a sufficient initial condition for the classical equation. However, with the new equation it may seem to be insufficient, since this equation contains second time derivative. It is shown in Ref. [23] that for the elliptic diffusion equation, without the convective and the entrapment terms, a sufficient additional condition is limitedness of the solution as $t \to \infty$. Obviously, this additional condition should also be fulfilled for our equation.

The fact, that initial Cauchy data $c(x, t = 0)$ together with the requirement for solution to be limited when time tends to infinity provides with unique solution of Eq. (12), can be illustrated by a simple example of uniform solution $c(t)$. It corresponds to the Brownian motion of particles in stagnant water saturated porous medium. Eq. (12) is reduced to an ordinary differential equation

$$\frac{\mathrm{d}c}{\mathrm{d}t} = D_t\frac{\mathrm{d}^2 c}{\mathrm{d}t^2} - \Lambda c$$

with uniform initial data

$$t = 0\text{: } c = c_0.$$

The solution is given by the formula

$$c = (c_0 - B)\exp\left[\left(\frac{1}{2D_t} - \sqrt{\frac{\Lambda}{D_t} + \frac{1}{4D_t^2}}\right)t\right] + B\exp\left[\left(\frac{1}{2D_t} + \sqrt{\frac{\Lambda}{D_t} + \frac{1}{4D_t^2}}\right)t\right]$$

where B is an arbitrary constant. Uniqueness of the solution requires an additional condition to determine the constant B.

The condition of limited concentration when t tends to infinity implies $B = 0$ resulting in a unique solution

$$c = c_0\exp\left[\left(\frac{1}{2D_t} - \sqrt{\frac{\Lambda}{D_t} + \frac{1}{4D_t^2}}\right)t\right].$$

The solution described decay of initial uniform particle distribution during Brownian motion in porous media due to particle capture by matrix.

For the advective-dispersive transfer of the tracer transport without capture, solution of the Riemann problem (25) on the large times approaches the solution of the problem of continuous tracer injection [9]. The last problem is stated on the semi-axis $x > 0$:

$$t = 0\text{: } c(x, 0) = 0, \qquad x > 0; x = 0: \quad c(0, t) = 1.$$

However, if capturing takes place, similarity between the two problems disappears, since capturing significantly reduces with time the value of the concentration at $x = 0$. Solution of the continuous injection problem will not be described in this work.

Another problem, which will be considered below, is the problem of the pulse injection. This problem may also be stated on the full axis $-\infty < x < \infty$:

$$t = 0\text{: } c(x, 0) = \delta(x). \tag{26}$$

Experiments on pulse injection are also often performed [8,11,16].

3.2. Analytical solution of the Riemann problem

Let us outline solution of the formulated problem. First, we apply Galilean transformation (20), selecting the such value of V that results in $D_{XT} = 0$. According to Eq. (22),

$$V = D_{xt}/2D_t.$$

Eq. (12) is reduced to

$$\frac{\partial c}{\partial T} + u\frac{\partial c}{\partial X} = D_X\frac{\partial^2 c}{\partial X^2} + D_T\frac{\partial^2 c}{\partial T^2} - \Lambda c, \tag{27}$$

with

$$X = x - Vt, \qquad T = t, \qquad u = v - D_{xt}/2D_t, \qquad D_X = D_x - D_{xt}^2/4D_t, \qquad D_T = D_t. \tag{28}$$

Further transformation aims at eliminating the first-order derivatives. We substitute

$$c = \mathrm{e}^{ax+bt}C, \quad a = u/2D_X, b = 1/2D_T.$$

The result of this substitution is the following equation for C:

$$D_X\frac{\partial^2 C}{\partial X^2} + D_T\frac{\partial^2 C}{\partial T^2} = \Lambda_1 C,$$
$$\Lambda_1 = \Lambda + \frac{1}{4D_T} + \frac{u^2}{4D_X}.$$

Finally, rescaling

$$\tau = t\sqrt{\Lambda_1/D_T}, \qquad \xi = x\sqrt{\Lambda_1/D_X}$$

leads to the standard Helmholtz equation:

$$C_{\xi\xi} + C_{\tau\tau} = C. \tag{29}$$

Initial conditions (25) are transformed to

$$C(\xi, 0) = \mathrm{e}^{-u\xi/2\sqrt{\Lambda_1 D_X}} \qquad (\xi < 0); \quad C(\xi, 0) = 0 \quad (\xi > 0). \tag{30}$$

Solution of Eq. (29) with boundary conditions (30) is obtained by application of the double layer potential [30]. Fundamental solution of Eq. (29) is the zero-order Bessel K-function $C_f(\xi, \tau) = K_0(r)$, $r = \sqrt{\xi^2 + \tau^2}$. Since it is an even function of τ, the double layer potential with density ρ for the upper semiplane has the form of

$$C_{dl}(\xi, \tau) = \int_{\tau'=0} \rho(\xi')\frac{\partial C_f}{\partial \tau}(\xi - \xi', \tau)\mathrm{d}\xi'.$$

On the boundary $\tau = 0$ the double layer potential is discontinuous:

$$C_{dl}(\xi, 0 + 0) = C_{dl}(\xi, 0) + \pi\rho(\xi).$$

The first addendum in the right-hand side of the last equation is equal to zero, since $\partial C_f/\partial\tau = 0$ at $\tau = 0$. Thus, in order to obey boundary conditions (30), it is necessary to select

$$\rho(\xi) = \mathrm{e}^{-u\xi/2\sqrt{\Lambda D_X}}/\pi \quad (\xi < 0); \qquad \rho(\xi) = 0 \quad (\xi > 0).$$

Performing back substitutions and transformations, we finally obtain the solution in the form of

$$c = \frac{\mathrm{e}^{t/2D_T}\Lambda_1}{\pi\sqrt{D_X D_T}}\int_{x-Vt}^{\infty} \frac{\mathrm{e}^{u\xi/2D_X}t}{\sqrt{\xi^2(\Lambda_1/D_X) + t^2(\Lambda_1/D_T)}} K_1\left(\sqrt{\xi^2(\Lambda_1/D_X) + t^2(\Lambda_1/D_T)}\right)\mathrm{d}\xi. \tag{31}$$

Here

$$V = D_{xt}/2D_t, \qquad u = v - V, \qquad D_X = D_x - D_{xt}^2/4D_t, \qquad D_T = D_t, \tag{32}$$
$$\Lambda_1 = \Lambda + \frac{1}{4D_T} + \frac{u^2}{4D_X}.$$

3.3. Solution of the pulse injection problem

Solution of the pulse injection problem (26) is obtained from the solution of the Riemann initial problem (25). Using temporarily the designations c_R and c_p for the solutions of the Riemann and of the pulse injection problems, correspondingly, we notice that the initial conditions for these problems are connected:

$$c_p(x, 0) = -\partial c_R(x, 0)/\partial x.$$

In view of linearity, the same is valid for the solutions:

$$c_p(x, t) = -\partial c_R(x, t)/\partial x.$$

Differentiation, after some transformations, results in

$$c_p = \frac{\mathrm{e}^{t/2D_T}\Lambda_1}{\pi\sqrt{D_X D_T}} \frac{\mathrm{e}^{u(x-Vt)/2D_X}t}{\sqrt{(x - Vt)^2(\Lambda_1/D_X) + t^2(\Lambda_1/D_T)}} K_1\left(\sqrt{(x - Vt)^2(\Lambda_1/D_X) + t^2(\Lambda_1/D_T)}\right). \tag{33}$$

The different coefficients in the last equation are defined by Eq. (32).

4. Sample calculations

The goal of this section is to show the typical behavior of the solutions of the pulse injection problem obtained on the basis of the elliptic transport equation, in comparison with the solutions of the common AD equation. Solution of the elliptic equation is given by Eq. (33), with the parameters defined in (32). The corresponding solution of the AD equation is expressed by

$$c_{AD} = \frac{\mathrm{e}^{-\Lambda t}}{2\sqrt{\pi D_x t}} \exp\left(-\frac{(x-vt)^2}{4D_x t}\right). \tag{34}$$

We investigate how the solutions vary depending on the transport coefficients and demonstrate that they can qualitatively predict the concentration behavior observed in the pulse injection experiments and are in a qualitative agreement with the solutions obtained previously in the framework of the CTRW theory and with the experimental observations.

4.1. Dimensionless parameters

In order to solve master equation (12) for the reasonable values of all the parameters, we bring it into the dimensionless form. Select T, L, C_0 as the characteristic values of time, length and concentration, correspondingly. Since the equation is linear with regard to concentration, C_0 is eliminated. Denoting the dimensionless variables by dashes, we bring the equation to the form of

$$\frac{\partial c'}{\partial t'} + \frac{vT}{L}\frac{\partial c'}{\partial x'} = \frac{D_x T}{L^2}\frac{\partial^2 c'}{\partial x'^2} + \frac{D_t}{T}\frac{\partial^2 c'}{\partial t'^2} + \frac{D_{xt}}{L}\frac{\partial^2 c'}{\partial x' \partial t'} - \Lambda T c'. \tag{35}$$

As usual, the values of L and T are selected in such a way that the dimensionless convective velocity becomes unity:

$$v = L/T.$$

We consider the case of convective, rather than molecular, dispersion, where coefficient D_x is given by Eq. (23). Denote by $\alpha = L/\alpha_D$ the ratio of the characteristic scales of the problem and of the heterogeneity. This is one of the dimensionless parameters of the problem. We select, correspondingly, L and T in such a way that (equivalently to Eq. (23))

$$D_x = Lv/\alpha = L^2/\alpha T.$$

From the last two conditions,

$$L = \alpha D_x/v, \qquad T = \alpha D_x/v^2.$$

Substitution of these relations into Eq. (34) results in

$$\frac{\partial c'}{\partial t'} + \frac{\partial c'}{\partial x'} = \frac{1}{\alpha}\left(\frac{\partial^2 c'}{\partial x'^2} + d_t \frac{\partial^2 c'}{\partial t'^2} + d_{xt}\frac{\partial^2 c'}{\partial x' \partial t'} - \gamma c'\right). \tag{36}$$

Thus, the equation contains the four dimensionless parameters: the heterogeneity parameter α; the ratios of different dispersion coefficients $d_t = D_t v^2/D_x$; $d_{xt} = D_{xt} v/D_x$; and the dimensionless capture rate $\gamma = \Lambda v^2/D_x$.

In the sample calculations, we assume that the last three parameters are of the order of unity. The heterogeneity ratio α may be an order of magnitude less than unity [32]. However, if it is too small, dispersion and capture may be neglected. We select it to be 0.1. The dimensionless capturing parameter γ may widely vary [13]. We will show, however, that it mainly rescales the solution and does not affect much its shape. Thus, most of the calculations are carried out for $\gamma = 0$. The dimensionless coefficients d_t, d_{xt} are taken to be unity and zero, correspondingly, and then vary when the dependence on them is investigated. The concentration profiles are plotted at the dimensionless time $t' = 0.5$. In the following, we omit dashes at the dimensionless variables. Slightly simplifying the language, we talk about the elliptic and the AD (or parabolic) solutions, meaning the solutions of the corresponding equations.

4.2. Results of the calculations

First, let us confirm the statement at the end of the previous section, namely, that the value of γ changes the values of the concentration, but does not significantly affect the shape of the curve. Sample calculations are presented in Fig. 1, for the value of γ varying between zero and ten. The maxima of the concentration profiles are not displaced, and the characteristic shapes of the curves are preserved.

A typical behavior of the solutions is illustrated in Fig. 2, where the solutions of the standard AD and of the elliptic transport equation are compared for the standard set of the governing parameters described above. Unlike the AD solution, the elliptic solution is highly asymmetric. Its maximum moves much slower than the maximum of the AD solution moving with the velocity of the flow. While at $t = 0.5$ and $v = 1$ the maximum of the AD solution is obviously located at $x = 0.5$, the maximum of the elliptic solution is at $x = 0.28$ — that is, it moves almost twice slower. The value of the maximum concentration is slightly lower for the elliptic solution. Later it will be shown that this is not a general rule. It is important that

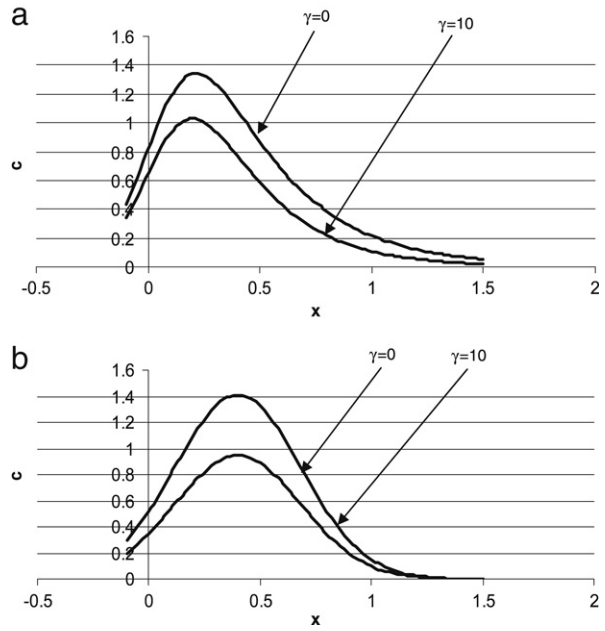

Fig. 1. Comparison of the solutions of the elliptic (a) and parabolic (b) transport equations under the different values of γ (see Eq. (36)).

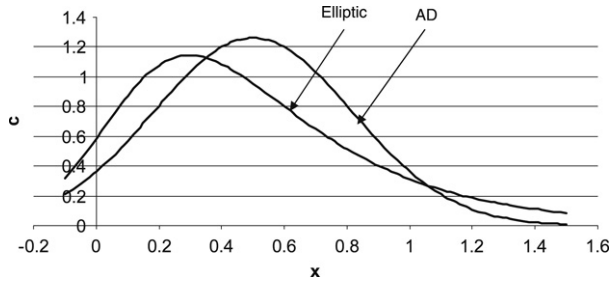

Fig. 2. Plots of the solutions of the elliptic and the classical AD equations for the standard set of the constituting parameters.

the forward "tail" of the elliptic solution is much more massive than the corresponding "tail" of the AD solution. Apparently, the elliptic equation separates the "slow" and the "rapid" particles much more than the classical parabolic AD equation. The "slow" particles form the maximum staying behind the flow, while the "rapid" particles move faster than the flow. Analysis described in Ref. [23] shows that the elliptic solution decreases at infinity as $x^{-3/2}e^{-\alpha x}$, while the parabolic solution decreases much faster, as $e^{-\beta x^2}$.

The observed difference between the solutions is important for practical applications, like measurements of the velocity of the flux by tracer propagation. In many cases velocity of the flux is evaluated by appearance of the first valuable portion of the tracer on the production side. The previous calculations show that this judgment may lead to overestimation of the flux velocity. Meanwhile, another estimate of the flux velocity, by arrival of the maximum of the tracer, may lead to its underestimation. Similar tendencies were observed in the laboratory [16] and in the large-scale experiments [10,11]. They are in a qualitative agreement with the predictions of the more complex version of the CTRW theory based on the solutions of the integral–differential equations [20].

Fig. 3 shows the dependence of the position of the maximum of the solution and the height on the maximum on the value of the dispersion coefficient d_{tt}. Recall that, while d_{tt} changes from 0 to 5, the dimensionless time dispersion coefficient $D_{tt} = \alpha d_{tt}$ changes from 0 to 0.5. The position of the maximum exhibits large variability, changing from $x_{\max} = vt$ at $D_{tt} = 0$ to $x_{\max} \approx 0.2vt$ at $D_{tt} = 0.5$. The height of the maximum varies in a narrower range. This variation is non-monotonous, and the height of the maximum may both be higher or lower than the corresponding value in the classical AD theory (the value at $d_{tt} = 0$).

Similar plots for the dependence of the maximum on the value of the mixed dispersion coefficient d_{xt} are shown in Fig. 4. Although the variation looks less pronounced, it is still rather strong. Recall that, while d_{xt} varies from -0.9 to 0.9, as in Fig. 4, coefficient D_{xt} changes only from -0.09 to 0.09. Under these conditions the position of the maximum changes almost two times. Variation of the height of the maximum is not that significant. It may be, again, both higher and lower than the maximum of the parabolic solution.

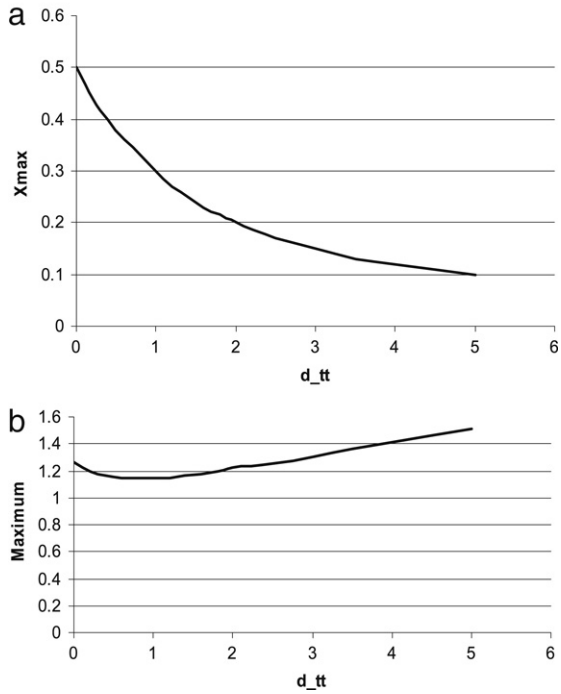

Fig. 3. Position of the maximum of the solution (a) and the value of the maximum (b) depending on the value of the time dispersion coefficient d_{tt}.

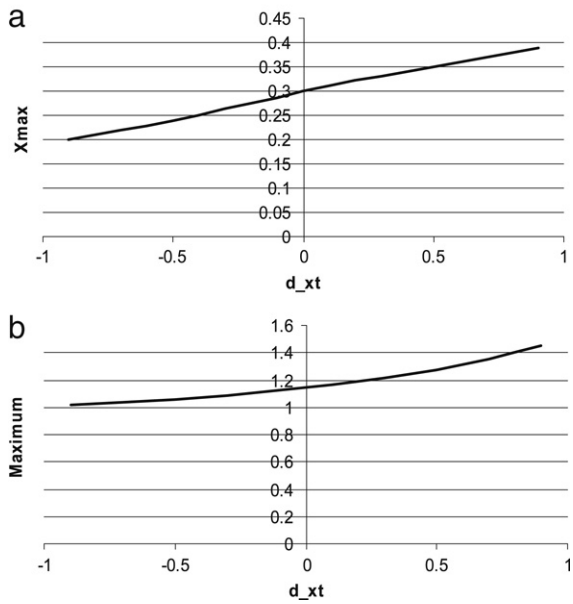

Fig. 4. Dependence of the position of the maximum (a) and its value (b) on the mixed dispersion coefficient d_{xt}.

Finally, Fig. 5 illustrates behavior of the "tails" of the two solutions. It shows the ratio of the values of the elliptic and the parabolic solutions at $x = 1.48$, where the "parabolic" value is equal to 1%. The "elliptic" concentration is almost ten times larger. For the most values of the time dispersion coefficient D_{tt} (from 0.08 to 0.5) this concentration varies between 8% and 9.6%.

5. Conclusions

We have derived a new description of transport of an ensemble of particles in a porous medium in the framework of the theory of the continuous time random walks (CTRW). We have shown that this unsteady-state process may be described

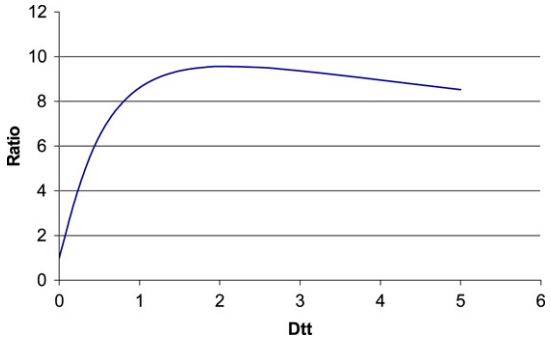

Fig. 5. Dependence of the ratio of elliptic and parabolic solutions at $x = 1.48$ (where the value of the parabolic solution is equal to 1%).

by the elliptic transport equation. This equation contains not only the standard dispersion term $D_x\partial^2 c/\partial x^2$, but also a new time dispersion and mixed dispersion terms, $D_t\partial^2 c/\partial t^2$, $D_{xt}\partial^2 c/\partial x\partial t$. The new equation describes transport of the tracers and colloids in porous media. In the last case, an additional precipitation term is introduced.

The properties of the new equation are investigated and its simplest solutions are obtained. It is shown that these solutions exhibit a similar behavior to much more complex solutions of the general CTRW theory, and that they are in agreement with the laboratory and the large-scale experimental observations. For the pulse injection problem, the maximum of the solution moves slower than the average flow velocity, while the forward "tail" contains much more particles than predicted by the classical advection-dispersion theory.

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Appendix A. Stochastic derivation of the master equation

The integral master equation has been postulated in Section 2 by extension of Einstein's simple physical arguments. The goal of this appendix is to derive this equation on the basis of the CTRW theory. In Appendix B we explain, following Ref. [23], why expansion up to second order terms is necessary for the right approximation of the solution in the limit of small steps, as described in Section 2. The derivations in this appendix are similar to the classical CTRW derivations [3,19,20]. A non-trivial difference is in introduction of the capture probabilities. That is why we have preferred repeat these derivations in a greater detail.

We consider the case where all the particles walk along the infinite axis, and initially they are concentrated at zero. Since the particles walk independently, a linear master equation obtained for this case is also true for arbitrary initial and boundary conditions.

Assume that a particle passes subsequently distances $l_1, \ldots, l_n \ldots$ over times $\tau_1, \ldots, \tau_n \ldots$, and the passing probabilities of the corresponding steps are $p_1, \ldots, p_n \ldots$. Each step (l_i, τ_i, p_i) is independent of other steps, although variables l_i, τ_i, p_i may be dependent for any fixed i. As in Section 2, $f(l, \tau, p)$ is mutual distribution of the three constituting variables in one step. We introduce also $f(l, \tau|p)$: the distribution density of l, τ under known p. For multiple steps, we introduce the corresponding multiple convolutions:

$$\begin{aligned} &f_n(X, T|p_1, \ldots, p_n) = (*)^n f(X, T|p_i) \\ &f_n(X, T, p_1, \ldots, p_n) = (*)^n f(X, T, p_i) = (*)^n f(X, T|p_i) \prod_{i=1}^{n} f(p_i). \end{aligned} \tag{37}$$

There is a methodological difficulty in the fact that the probability p_i is a distributed parameter and possesses a distribution density. Formally, this is a situation of the "randomized distributions" [27]. Hence, it is more rigorous to work with conditional densities $f_n(X, T|p_1, \ldots, p_n)$. We will often neglect this rigorousness for simplification of the derivations, which are rather elaborate anyway. Another simplification will be an assumption that the particles do not move continuously, but jump instantaneously to a new position $x_n = l_1 + l_2 + \cdots + l_n$ in subsequent time moments $t_n = \tau_1 + \tau_2 + \cdots + \tau_n$. A more realistic assumption that the particles move with constant velocities l_i/τ_i between these moments would add complexity without changing the result.

Let I_n be an event that a particle was not caught during the first n steps, and J_n an event that a particle is caught exactly at the nth step. Probability of I_n under known p_i is $p_1 \ldots p_n$, and probability of J_n is $p_1 \ldots p_{n-1}(1 - p_n)$. The particles occurring

at the interval $(x, x+\delta x)$ at time t are exactly all the particles which came to this point in one, two…n steps, but did not run further. Thus, their total number $c(x,t)\delta x$ is expressed as infinite sum

$$c(x,t)\delta x = \sum_{n=0}^{\infty} \int [\mathbf{P}\{x < x_n < x+\delta x, t_n < t, I_n | p_1, \ldots, p_{n+1}\} - \mathbf{P}\{x < x_n < x+\delta x, t_{n+1} < t, I_{n+1} + J_{n+1} | p_1, \ldots, p_{n+1}\}] \prod_{i=1}^{n+1} f(p_i)\mathrm{d}p_i.$$

The minuend in the last expression is the number of particles that have come to $(x, x+\delta x)$ at time moment $t_n < t$. The subtrahend is the number of particles that either have left the interval, making the next step before time t, or were captured before this time. Under condition $p_1, \ldots, p_{n+1}$ both event I_n and $I_{n+1} + J_{n+1}$ occur with probability $p_1 \ldots p_n$. Thus, the last expression may be represented as

$$c(x,t)\delta x = \sum_{n=0}^{\infty} \int \mathbf{P}\{x < x_n < x+\delta x, t_n < t | p_1, \ldots, p_n\} \prod_{i=1}^{n} p_i f(p_i)\mathrm{d}p_i - \sum_{n=0}^{\infty} \int \mathbf{P}\{x < x_n < x+\delta x, t_{n+1} < t | p_1, \ldots, p_{n+1}\} \prod_{i=1}^{n} p_i f(p_i)\mathrm{d}p_i f(p_{n+1})\mathrm{d}p_{n+1}. \quad (38)$$

Transform the probabilities under the integral sign of the last expression, integrating over time t (integration is carried out over $\mathrm{d}t'$):

$$\mathbf{P}\{x < x_n < x+\delta x, t_n < t | p_1, \ldots, p_n\} = \int_0^t \mathbf{P}\left\{x < x_n < x+\delta x, t' < t_n < t' + \mathrm{d}t' | p_1, \ldots, p_n\right\}.$$

In the second probability participating in expression (38), we separate the probability of the last step, taking into account that its distribution is independent of the previous steps:

$$\mathbf{P}\{x < x_n < x+\delta x, t_{n+1} < t | p_1, \ldots, p_{n+1}\} = \int_0^t \mathbf{P}\left\{x < x_n < x+\delta x, t' < t_n < t' + \delta t' | p_1, \ldots, p_n\right\} \mathbf{P}\{\tau_{n+1} < t - t' | p_{n+1}\}.$$

Now, probability $\mathbf{P}\left\{x < x_n < x+\delta x, t' < t_n < t' + \mathrm{d}t' | p_1, \ldots, p_n\right\}$ is, simply, $\delta x \mathrm{d}t' f_n(x, t' | p_1, \ldots, p_n)$. Meanwhile, $\mathbf{P}\{\tau_{n+1} < t - t' | p_{n+1}\}$ is $F(t - t' | p_{n+1})$. Grouping the addenda back we obtain the following expression for concentration:

$$c(x,t) = \left[\int f_n(x, t | p_1, \ldots, p_n) \prod_{i=1}^{n} p_i f(p_i)\mathrm{d}p_i\right] * \left[1 - \int F(t | p_{n+1}) f(p_{n+1})\mathrm{d}p_{n+1}\right].$$

Here we do not distinguish between convolutions by one or by two variables, since this is clear from context. Introducing function s and average probability P as in Eq. (10), we can rewrite the last equation in the form of

$$c(x,t) = \sum_{n=0}^{\infty} P^n \left((*)^n s(x,t)\right) * (1 - F(t)). \quad (39)$$

Here $F(t)$ is the distribution function of time corresponding to the distribution density $f(\tau)$. Now, in order to derive the integral master equation in the form of (9), we apply to both sides of the last equation operation $(\delta(x,t) - Ps(x,t))*$. As a result, sum $\sum_{n=0}^{\infty} P^n ((*)^n s(x,t))$ cancels out, and we obtain the equation in the form of

$$c(x,t) - Ps(x,t) * c(x,t) = \delta(x)\left[1 - F(t)\right].$$

The last equation is equivalent to Eq. (9) except for the expression in the right-hand side. This expression is important only at $x = 0$ and very small t (in fact, as will be shown later, it tends to zero at the limit $T_0 = \langle\tau\rangle_p \to 0$).

Appendix B. Proof of the expansion

As discussed at the end of Section 2.1, an open question in the derivation of the differential master equation (6) or (12) is why the expansion of the integral master equation (9) should stop at the second order. The goal of this appendix is to provide a ground for such an expansion. We follow the method previously developed for "pure" diffusion, referring to Ref. [23] and applying fundamental concepts of the stochastic semigroups [27].

As in Ref. [27], for each distribution density $g(l,\tau)$ we introduce the convolution operator $\mathbf{G}$: for any bounded function $u(x,t)$

$$\mathbf{G}u = \int u(x-l, t-\tau) g(l,\tau)\mathrm{d}l\mathrm{d}\tau.$$

The master equation (9) has the form of

$$c = P\mathbf{S}c,$$

and Eq. (39)

$$c(x,t) = \sum_{n=0}^{\infty} P^n \mathbf{S}^n \cdot \delta(x)(1-F(t)). \tag{40}$$

As discussed in Section 2.1, we consider the limit of infinitely small steps. That is, instead for single operator $\mathbf{S}$ and probability P we consider their family, such that time expectation $\langle\tau\rangle_p = T_0$ of a single step tends to zero and other values behave according to Eq. (14). Let us parametrize this family by T_0. We assume that as T_0 tends to zero

$$\frac{\mathbf{S}-\mathbf{1}}{T_0} \to \mathbf{U}, \qquad \frac{1-P}{T_0} \to \Lambda. \tag{41}$$

We assume, additionally, that

$$\frac{1-F(t)}{T_0} \to g(t). \tag{42}$$

The expression on the left-hand side is a monotonously decreasing distribution density. Therefore, the same is valid about the right-hand side. If convergence (42) does not take place, we can always select a converging subsequence [27]. A stronger statement that $(1-F(t))/T_0 \to 0$, $t > 0$, is not always valid: consider, for example, the distribution equal to zero and one with probabilities $1-p$ and p, correspondingly, and with $p \to 0$ (see, however, discussion below).

According to Ref. [27], Chapter IX, Section 3, Lemma 4, in this case for any sequence of numbers n such as $nT_0 \to t$

$$\mathbf{S}_{T_0}^n \to \exp(t\mathbf{U})$$

and, of course,

$$P^n \to \exp(-\Lambda t).$$

Eq. (40) in the limit considered may be represented as

$$c(x,t) \sim \sum_{n=0}^{\infty} \exp(-\Lambda n T_0)\exp(nT_0\mathbf{U})T_0 \cdot \delta(x)g(t).$$

It may be noted that the right-hand side of the last equation has the form of an integral sum. As $T_0 \to 0$, this sum is transformed to

$$c(x,t) = \int_0^{\infty} \exp(-\Lambda\tau)\exp(\mathbf{U}\tau)\mathrm{d}\tau \cdot \delta(x)g(t).$$

Application of the operator $-\Lambda\mathbf{1}+\mathbf{U}$ to the last equation results in

$$\begin{aligned}(-\Lambda\mathbf{1}+\mathbf{U})c &= \int_0^{\infty} (-\Lambda\mathbf{1}+\mathbf{U})\exp(-\Lambda\tau)\exp(\mathbf{U}\tau)\mathrm{d}\tau \cdot \delta(x)g(t)\\ &= \int_0^{\infty} \frac{\mathrm{d}}{\mathrm{d}\tau}[\exp(-\Lambda\tau)\exp(\mathbf{U}\tau)]\mathrm{d}\tau \cdot \delta(x)g(t) = \exp(-\Lambda t)\exp(Ut)|_0^{\infty} \cdot \delta(x)g(t)\\ &= -\delta(x)g(t).\end{aligned}$$

We have proven that in the limit of infinitely small steps the transport equation has the form of

$$\mathbf{U}c - \Lambda c = -\delta(x)g(t). \tag{43}$$

The next task is to prove that the differential operator $\mathbf{U}$ has the same form as in Eq. (12):

$$\mathbf{U}c = -\frac{\partial c}{\partial t} - v\frac{\partial c}{\partial x} + D_x\frac{\partial^2 c}{\partial x^2} + D_t\frac{\partial^2 c}{\partial t^2} + D_{xt}\frac{\partial^2 c}{\partial x \partial t}. \tag{44}$$

For the proof, we apply the results obtained in Ref. [27], Chapter IX and further. It is shown there that (generalizing onto the two dimensions) the general infinitesimal operator $\mathbf{U}$ for a continuous stochastic semigroup has the form of

$$\mathbf{U}C = -\frac{\partial C}{\partial t} - v\frac{\partial C}{\partial x} + \int \frac{C(x-\xi,t-\tau) - C(x,t) + \tau\partial C(x,t)/\partial t + \xi\partial C(x,t)/\partial x}{\xi^2+\tau^2}\Omega(\mathrm{d}\xi,\mathrm{d}\tau).$$

Here v has the same meaning as in Eq. (14); the fact that the coefficient at $\partial C/\partial t$ is minus unity is related to the fact that we divide by T_0 in the limit (34).

The last expression for **U** is reduced to Eq. (44) if and only if the dispersion measure Ω is concentrated at zero. On the other hand, analysis of the Fokker–Plank–Kolmogorov–Feller equation shows that measures Ω concentrated at zero correspond to the processes with continuous trajectories, while the trajectories of the processes with all the other possible measures Ω are discontinuous [27]. For our process, it is evident that its trajectories in the limit of infinitely small steps are continuous. Thus, it is physically reasonable to assume that measure Ω is concentrated at zero, and operator **U** has the form (44).

Infinitesimal measure $\Omega(\mathrm{d}\xi, \mathrm{d}\tau)$ is obtained as a limit [27]

$$\Omega(\mathrm{d}\xi, \mathrm{d}\tau) = \lim \frac{1}{T_0}(\xi^2 + \tau^2) f(\xi, \tau).$$

If this measure is concentrated at zero, it follows, in particular, that

$$\lim \frac{1}{T_0}\tau^2 f(\tau)\mathrm{d}\tau = A\delta(\tau)\mathrm{d}\tau.$$

(Convergence is always understood as a convergence of the measures, but not of the densities — see [27] for details.) It is easy to prove based on the last equality that function g determined by Eq. (42) is also equal to $\delta(t)$. Thus, the right-hand side of Eq. (43) is concentrated at zero, and this equation is reduced to Eq. (12). The proof is finished.

Appendix C. Derivation of the formula for the deposition rate

The goal of this appendix is to provide a direct stochastic derivation of the expression for the deposition rate discussed in Section 2.5. Similar to Eq. (38), the number of particles $R(x, t)\delta x\delta t$ entrapped at the interval δx during the time δt can be expressed as:

$$R(x, t)\delta x\delta t = \sum_{n=0}^{\infty} \int P_n(1 - p_{n+1})\mathbf{P}\{x < x_n < x + \delta x, t < t_n < t + \delta t | p_1, \ldots, p_{n+1}\} \prod_{i=1}^{n+1} f(p_i)\mathrm{d}p_i.$$

This equation may be transformed fully similar to the expression for $c(x, t)$, resulting at

$$R(x, t) = (1 - P) \sum_{n=0}^{\infty} P^n s^{(*n)}(x, t). \tag{47}$$

This equation is, in turn, is to be compared with Eq. (39) for $c(x, t)$. Multiplying Eq. (39) by $\Lambda \approx (1 - P)/T_0$, we obtain

$$\Lambda c(x, t) = (1 - P) \sum_{n=0}^{\infty} P^n \left((*)^n s(x, t)\right) * \frac{1 - F(t)}{T_0}.$$

As discussed at the end of Appendix B, $(1 - F(t))/T_0 \to \delta(t)$ as $T_0 \to 0$. Thus, the whole expression converges to Eq. (47) for $R(x, t)$. Equality $R = \Lambda c$ is proven.

References

[1] S. Pang, M.M. Sharma, SPE paper 28489, 1994.
[2] K.E. Wennberg, M.M. Sharma, SPE paper 38181, 1997.
[3] B. Berkowitz, A. Cortis, M. Dentz, H. Scher, Reviews of Geophysics 44 (2006) 1–49. RG2003.
[4] A.C. Payatakes, C. Tien, R.M. Turlan, AIChE Journal 19 (1) (1973) 58–76.
[5] A.C. Payatakes, R. Rajagopalan, C. Tien, The Canadian Journal of Chemical Engineering (1974) 52–62.
[6] M. Elimelech, J. Gregory, X. Jia, R.A. Williams, Particle Deposition and Aggregation, Butterworth-Heinemann, USA, 1995.
[7] K. Khilar, S. Fogler, Migration of Fines in Porous Media, Kluwer Academic Publishers, Dordrecht, London, Boston, 1998.
[8] E.A. Sudicky, R.W. Gillham, E.O. Frind, Water Resources Research 21 (7) (1985) 1035–1041.
[9] S.E. Silliman, E.S. Simpson, Water Resources Research 23 (8) (1987) 1667–1673.
[10] J.M. Boggs, S.C. Young, W.R. Waldrop, R.W. Gelhar, E.E. Adams, K.R. Rehfeldt, Atomic Energy of Canada Limited Report, 1 10308, 1190, pp. 34–56.
[11] G. Kosakowski, B. Berkowitz, H. Scher, Journal of Contaminant Hydrology 47 (2001) 29–51.
[12] T. Iwasaki, Journal of American Water Works Association (1937) 1591–1602.
[13] J.P. Herzig, D.M. Leclerc, P. le Goff, Industrial and Engineering Chemistry 62 (8) (1970) 8–35.
[14] A.A. Shapiro, P.G. Bedrikovetsky, A. Santos, O.O. Medvedev, Transport in Porous Media 67 (2007) 135–164.
[15] A. Dieulin, G. Matheron, G. de Marsily, The Science of the Total Environment 21 (1981) 319–328.
[16] M. Levy, B. Berkowitz, Journal of Contaminant Hydrology 64 (2003) 203–226.
[17] N. Tufenkji, J.A. Redman, M. Elimelech, Environmental Science & Technology 37 (2003) 616–623.
[18] N. Tufenkji, M. Elimelech, Langmuir 20 (2004) 10818–10828.
[19] E.W. Montroll, B.J. West, in: E.W. Montrol, J.L. Leibowitz (Eds.), Fluctuation Phenomena, North-Holland Publishing Company, 1979, pp. 62–175. (Chapter 2).
[20] B. Berkowitz, H. Scher, Transport in Porous Media 42 (2001) 241–263.
[21] A. Cortis, Physical Review E 76 (2007) 030102(R).
[22] A. Cortis, Y. Chen, H. Scher, B. Berkowitz, Physical Review E 70 (2004) 041108.
[23] A.A. Shapiro, Physica A 375 (2007) 81–96.
[24] A. Einstein, Annalen der Physik 17 (1905) 549–560.
[25] C.W. Gardiner, Handbook of Stochastic Methods, Springer, Berlin, 2002.
[26] F.A.L. Dullien, Porous Media. Fluid Transport and Pore Structure, Academic Press, New York, 1979.
[27] W. Feller, An Introduction to Probability Theory and Its Applications, vol. II, Wiley, New York, 1979.
[28] P.V. Zhelezny, A.A. Shapiro, Journal of Porous Media 9 (4) (2006) 275–289.
[29] V.I. Selyakov, V.V. Kadet, Percolation Models for Transport in Porous Media, Kluwer Academic Publishers, Dordrecht, 1996.
[30] A.N. Tikhonov, A.A. Samarskii, Equations of Mathematical Physics, Pergamon Press Ltd., Oxford, England, 1963.
[31] J.F. Altoé, P.G. Bedrikovetsky, A.G. Siqueira, A.L.S. de Souza, F.S. Shecaira, Journal of Petroleum Science and Engineering 51 (2006) 68–84.
[32] V.N. Nikolaevskiy, Geomechanics and Fluidodynamics, Kluwer Academic, Dordrecht, Boston, London, 1996.