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Chapter 1

APPLICATION OF STOCHASTIC APPROACHES TO MODELING SUSPENSION FLOW IN POROUS MEDIA

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Abstract

The goal of this chapter is to overview several stochastic approaches to modeling suspension flows in porous media, including the population balance approach, the continuous time random walk (CTRW) approach, and its reduction to the elliptic equation approach. Most of these approaches emerged recently, although their mathematical background is relatively well-known. Some problems (like upscaling) require the development of new methods. The connections between the formalisms, the discrepancies between them and their capabilities are analyzed and compared. Comparison to experimental data is also briefly discussed. The population balance models growing out of the Boltzmann-Smolukhowski formalism take into account the particle and the pore size distributions. A system of integral-differential kinetic equations for the particle transport is derived and averaged. The continuous-time random walk theory considers the distribution of the residence times of particles in pores. The transport equation derived in the framework of CTRW contains a convolution integral with a memory kernel accounting for the particle flight distribution. An important simplification of the CTRW formalism, its reduction to an elliptic transport equation, is also discussed. The CTRW approach and the elliptic equation are both able to catch abnormal behavior of suspended particles, such as the algebraic decaying tail in the breakthrough curve or asymmetric particle distribution from a pulse injection. The elliptic equation approach can be generalized onto poly-disperse particle and pore systems, just incorporating the characteristic features and advantages of both CTRW and population balance approaches.

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1. Introduction

Flow of particulate suspensions in various types of porous media appears in a large variety of industrial and natural processes of practical importance. The literature discusses different problems of petroleum engineering; ground water flows; industrial filtration; chromatography; migration of bacteria and viruses; different types of ecological problems; and other [1-4]. Filtration is a complex process involving particle dispersion in the flux, deposition and mobilization, modification of the porous medium and permeability decline. There is a considerable and ongoing effort aimed at understanding these processes. Recently, the population balances of size-distributed particles, non-Fickian transport of the particle populations and various non-trivial cases of their deposition have attracted significant interest [5-11].

The conventional approach to modeling transport in porous media usually involves a parabolic advection-dispersion equation (ADE) with a sink term representing the deposition from the suspended population into the retained solid phase (we do not consider the possibility for particle release) [1, 12]:

$$\phi \frac{\partial c}{\partial t} + U \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} - \lambda c; \tag{1}$$

$$\frac{\partial s}{\partial t} = \lambda c \tag{2}$$

This system describes the mass balance in terms of the averaged concentrations of suspended (flowing) particles c and deposited particles s. Deposition of the particles is treated similarly to the first order chemical reaction. There are different expressions in the literature for the deposition coefficient λ depending on particular forces acting between the flow, the particles and internal surface of the porous medium [1, 3, 4, 13]. The transport of suspended particles is characterized by advection $U\partial c / \partial x$ and dispersion (diffusion) $D\partial^2 c / \partial x^2$. Throughout this chapter, we consider flows in single dimension x. Generalization onto multiple dimensions is, in most cases, trivial. The ADE system in one dimension can be solved, analytically or numerically, given initial conditions for c and s, and two boundary conditions [14, 15].

Since the dispersion term follows the Fickian description for mass transfer, the ADE is also referred to as the Fickian approach to modeling mass transport in porous media. The correspondence between the macroscopic description of Fickian transport and the random particle motion was established in the classical works on random walks [16-19]. It is a common belief in the hydrodynamic community that the effect of particle random walks is adequately described by the classical Fick-Einstein approach, and that the standard "parabolic" dispersive term is sufficient for taking into account this effect. However, more advanced studies of the random walks contradict this statement [20-25]. The reason is that the classical Einstein approach takes into account dispersion of the space walks, but not of the times of flight of the particles.

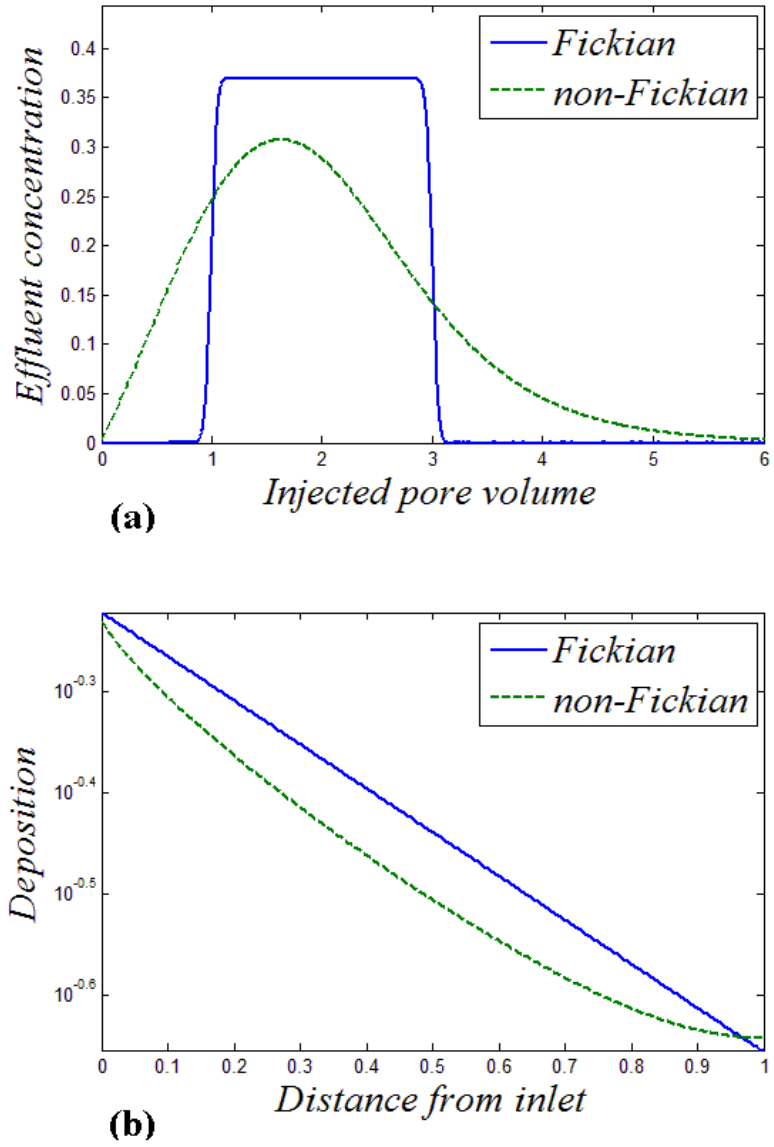

Figure 1. Qualitative shapes of breakthrough curves and deposition profiles for Fickian and non-Fickian transport.

Disagreement between model outputs from the ADE and the experimental observations has been reported in a number of works [5-9, 26, 27]. The two curves are measured in a typical filtration experiment: the deposition profile (distribution of the deposited particles along a sample of the porous medium) and the breakthrough curve (production of the particles at the outlet of the sample with time), as seen in Figure 1. The model parameters in the ADE are usually estimated by fitting the output effluent concentration profiles/breakthrough curves to the experimental data. The deposition profiles are attempted to be predicted by the application of the parameters estimated by fitting the breakthrough curves. This program has not always been successful. For example, in Refs. [26-30], the early arrival and the delay of

particles at the outlet of the sample were observed, in contradiction to the predictions of the ADE approach. Deviations in behavior of the particles in the flow from the Fickian picture are commonly attributed as anomalous, or non-Fickian diffusion. The classical theory predicts exponential or almost exponential deposition profiles. Contrary to it, in Refs [5-9, 31] the hyper-exponential (steeper than exponential) and non-monotonic deposition profiles were observed. Thus, both breakthrough curves and deposition profiles may deviate from the predictions of the ADE theory.

The discrepancies between the ADE and experiments have been explained by the following reasons: (i) Already mentioned distribution of particle flights in the flow and particle residence times in pores related to the median heterogeneity of the porous medium, and (ii) Heterogeneity of particle-medium interactions caused by the difference between the different particles in the population (e.g. of the particle sizes or surface charges), by distribution of the pore sizes, and by heterogeneity of the internal porous surface.

The process of particle/solute transport in porous media is stochastic in nature. Motion of the suspended particles is random. Parameters of particles and pores are usually widely distributed. Interactions between particles and pores may be caused by the different physical mechanisms, such as surface attachment via primary or secondary energy minima, straining at pore constrictions, size exclusion, bridging, gravity deposition [3, 5, 6, 32-34]. Modeling of the random motion of the particles and the heterogeneous interactions between particles and pores calls for stochastic approaches.

Several stochastic models of transport in porous media emerged recently. The population balance models based on the Boltzmann-Smolukhowski approach took into account the particle and the pore size distributions [34-39]. This approach focuses on factor (ii) described above (heterogeneity of the particle-pore system), but does not account for factor (i) (distribution of the residence times). A system of integral-differential kinetic equations is derived for particle transport. Its averaging makes it possible to produce a system of differential transport equations for the particles. The approach is described in Section 2 below.

The continuous-time random walk (CTRW) theory has been applied to model monodisperse colloids/tracer transport in porous media [11, 27, 37, 40-46]. In Refs. [26, 27, 40-43, 47-49], the authors derived a transport equation for the particles, analyzed it by means of the Laplace transform and applied to the different experimental data and practical problems. The transport equation contained the convolution integral with a memory kernel accounting for particle flight distribution (factor (i) above). The CTRW approach was proved to be able to catch abnormal behavior of suspended particles, such as the algebraic decaying tail in the breakthrough curve or asymmetric particle distribution from a pulse injection [26, 40, 41, 43, 49]. To the best of our knowledge, no generalization of the straightforward CTRW approach onto the distributed particle populations has been presented in the literature, although such generalization may be straightforward for some cases (e.g. for dilute suspensions). Thus, factor (ii) has remained uncovered by the model.

An important simplification of the CTRW formalism has been its reduction to an elliptic transport equation or a system of such equations. This reduction is possible in the limit of many infinitely small flights, for reasonably bounded particle flight distributions [44, 45]. This approach is described in Section 4. Compared to the ADE, the elliptic equation includes an additional second order derivative to time and a mixed derivative accounting for the distribution of the particle residence times. It has been shown that the version of the CTRW based on the elliptic equation predicts behavior similar to the “full-scale” version of the

CTRW [50]. Recently, the model has been extended onto the case of the distributed particles, thus accounting not only for factor (i), but also for factor (ii) above [50]. The model has been thoroughly compared to experimental data [11, 46].

It should be mentioned that the mathematical models of filtration may also be applied to flows of tracers, or neutral low-concentrated additives, in porous media. Tracers are widely used in practical applications, e.g. to study connectivity of the petroleum reservoirs or directions and rates of the underground flows [51-53]. Motion of the tracers is driven by similar physical mechanisms to the particles with slightly different dispersion and deposition behavior (or, often, with no deposition at all). That is why the models for deep bed filtration may be tested on the experimental data obtained for the tracer flows.

2. Population Balance Approach

The population balance approach originates in the works of Boltzmann on the gas kinetic theory and the subsequent work of Smolukhowski, who applied a similar formalism to the problem of particle coagulation [54]. In the approach to deep bed filtration developed in papers [34-37, 39], the particles and the pores are described as the two populations (ensembles) distributed by the particle sizes r_s and pore sizes r_p (it should be remarked that by "sizes" one may understand not only geometrical sizes, but also other physical parameters or even their sets). "Collisions" between particles and pores may result in passing through or entrapping a particle.

Probably, the first population balance model for deep bed filtration was suggested in work [38]. In our discussion, we mainly follow paper [37], where, to the best of our knowledge, the formalism was, apparently, first described in its present form. Several modifications and extensions of the formalism were suggested in paper [39].

2.1. Constituting Equations

2.1.1. Particle Flow Characteristics

As mentioned in the Introduction, our goal is to discuss the mathematical structure of the theory in some simplifying physical assumptions. The assumption taken in this section is that the particle sizes are much smaller than the pore sizes. These conditions are characteristic of many experimental works [5-8, 55-58]. This eliminates the volumetric and velocity corrections to the particle flow, which become important for the particles, whose sizes are comparable to the pore sizes and may result in the fractional-flow filtration theories of the different kinds [34, 37, 39]. An opposite case, where the particle sizes are comparable to the pore sizes, and when the deposition is caused by the size exclusion mechanism, may also be considered in the framework of the described formalism [34-36].

Any model of deep bed filtration involves the two types of characteristics. The a priori characteristics (the constituting dependences and parameters) are assumed to be known in advance and invariable in the course of the filtration. The variable characteristics obey a system of kinetic balance equations to be derived.

Under the assumption above, the main a priori characteristic in the proposed model is the particle-pore interaction probability $p\left(r_s, r_p \to r_p^{'}\right) dr_p'$: a probability of the event that a particle of the size r_s is captured in a pore of the size r_p, as a result of which the pore size changes to r_p'. Such a probability takes into account a possibility of incomplete plugging of a pore after particle capture. The distribution function $p\left(r_s, r_p \to r_p^{'}\right)$ possesses the following properties:

$$\begin{aligned} p\left(r_s, r_p \to r_p'\right) = 0: \;\; r_p \le r_p'; \\ \int_0^\infty p\left(r_s, r_p \to r_p'\right) dr_p' = p\left(r_s, r_p\right) \end{aligned} \tag{3}$$

where $p(r_s, r_p)$ is a probability of capturing a particle r_s at a pore r_p, which will also be used in the following.

Another a priori characteristics is the reference (correlation) length of the porous medium L. This is, essentially, an adjustment parameter determining the spatial frequency of particle-pore "collisions". In Ref. [39], a model porous medium has been described as a system of "paths" and "chambers". The particles move along the paths and mix in the chambers. The value of L is defined as a characteristic distance between the two chambers.

Let us define now the variable functions to be determined. The classical filtration theory [3, 59] describes the transport of suspended particles in terms of the averaged concentration per unit pore volume, $c(x,t)$. It does not distinguish between the particles of different sizes. The population balance approach [34, 35, 37, 39, 50] adopts more detailed characteristics, e.g. the particle size distribution $C(r_s,x,t)$ by the values of r_s:

$$c(x,t) = \int C(r_s, x, t) dr_s; \quad f(r_s, x, t) = \frac{C(r_s, x, t)}{c(x,t)} \tag{4}$$

where $f(r_s,x,t)$ is the distribution density of the suspended particles. The ensemble of pores is characterized by their distribution by sizes r_p:

$$h(x,t) = \int H\left(r_p, x, t\right) dr_p; \quad f\left(r_p, x, t\right) = \frac{H\left(r_p, x, t\right)}{h(x,t)} \tag{5}$$

where $h(x,t)$ is the number of pores per unit cross-section of porous media, $H(r_p,x,t)$ and $f(r_p,x,t)$ are the pore size distribution by r_p and the corresponding distribution density. The two distributions, $C(r_s, x, t)$ and $H(r_p, x, t)$, vary with time due to flow and deposition of the different particles. The balance equations for these ensembles are further derived.

2.1.2. Particle Flow Kinetics

The mass balance equation for the particles of a given size in one dimension can be written as [34, 35, 37]:

$$\frac{\partial\phi(x,t)C(r_s,x,t)}{\partial t}+\frac{\partial Q(r_s,x,t)}{\partial x}=-\frac{\partial\Sigma(r_s,x,t)}{\partial t} \tag{6}$$

where $\phi(x,t)$ is the porosity, $Q(r_s,x,t)$ is the flux of particles, and $\Sigma(r_s,x,t)$ is the concentration of deposited particles of r_s. For particles much smaller than pores, we do not have to introduce the porosity $\phi(r_s,x,t)$ accessible for particles of r_s, as done, for example, in [37]. The flux of particles may be expressed as the total flow of particles through all of the pores at a unit surface [37]:

$$Q(r_s,x,t)=C(r_s,x,t)\int q(r_p,x,t)H(r_p,x,t)dr_p \tag{7}$$

Here, $q(r_p,x,t)$ is the average flow rate through a pore of the size r_p. In assumption that the particles are much smaller than pores, the flux expression may be simplified to:

$$Q(r_s,x,t)=UC(r_s,x,t) \tag{8}$$

where U is the average fluid velocity. More sophisticated expressions accounting for incomplete accessibility of the pore space and the velocity corrections for the particles of different sizes are discussed in [34, 35, 37, 39].

2.1.3. Particle Capture Kinetics

The particle capture rate is usually assumed to be proportional to the frequency of collisions between particles and pores [34, 35, 37, 50]. Providing that the capture probability of a particle r_s in the pore, r_p is $p(r_s,r_p)$, the kinetic equation for the particle capture can be expressed by [37]:

$$\frac{\partial\Sigma(r_s,x,t)}{\partial t}=C(r_s,x,t)\frac{1}{L}\int_0^\infty p(r_s,r_p)q(r_p,x,t)H(r_p,x,t)dr_p \tag{9}$$

Eq. (9) is based on the assumption that particles coming to the pores are distributed independently of the pore sizes. It is similar to the Boltzmann assumption about “molecular chaos” [60].

The equation above requires an expression for the flow rate $q(r_p, x, t)$ in a single pore. In the simplest case of the parallel flows in the different flows in a cross-section, this expression is given by [37]:

$$q(r_p, x, t) = \frac{k_1(r_p)}{K(x,t)} U = \frac{k_1(r_p) U}{\int_0^\infty k_1\left(r_p\right) H\left(r_p, x, t\right) dr_p} \tag{10}$$

Here, $K(x,t)$ is the total permeability of the porous medium, which generally may vary due to the particle deposition. The value of $k_1(r_p)$ is a conductivity of a single pore (capillary) with regards to the flow. For example, for the Hagen-Poiseuille flow in a cylindrical capillary, $k_1(r_p) = \pi r_p^4 / 8$. More complicated effective medium-based or percolation-based schemes of permeability may also be suggested [38, 61].

A special role of the characteristic distance L in integral (9) should be discussed. The value of L arises from the fact that the deposition equation (9) (and the balance equation (6)) is written for the unit of *volume*, while the pore concentration $H(r_p, x, t)$ is the amount of pores per unit *cross-section*. In principle, the value of L should be distributed. However, this is difficult to introduce in the framework of the "pure" population balances. The distribution of L is partly reflected by the distribution of the particle flights introduced in the framework of the CTRW approach.

2.1.4. Pore Plugging Kinetics

Generally, a variation of the number of pores of a given size in a cross-section may be represented as a difference between the increase and decrease terms [37]:

$$\frac{\partial H\left(r_p, x, t\right)}{\partial t} = I\left(r_p, x, t\right) - D\left(r_p, x, t\right) \tag{11}$$

The value of $H(r_p, x, t)$ increases if a larger pore captures a particle and acquires size r_p. $H(r_p, x, t)$ decreases if a pore of the size r_p captures a particle and becomes smaller. In the assumption about independence of the particle and the pore characteristics prior to collision, the increase term $I\left(r_p, x, t\right)$ and the decrease term $D\left(r_p, x, t\right)$ can be expressed in the form

$$I\left(r_p, x, t\right) = \int_{r_p}^\infty dr_p' \int_0^\infty dr_s \left\{ p\left(r_s, r_p' \to r_p\right) q\left(r_p, x, t\right) H\left(r_p, x, t\right) C\left(r_s, x, t\right) \right\} \tag{12}$$

$$D\left(r_p, x, t\right) = \int_0^\infty dr_s \int_0^{r_p} dr_p' \left\{ p\left(r_s, r_p \to r_p'\right) q\left(r_p, x, t\right) H\left(r_p, x, t\right) C\left(r_s, x, t\right) \right\} \tag{13}$$

By integration over $r_p^{'}$, Eq. (13) can then be reduced to (cf. Eq.(3)):

$$D\left(r_p,x,t\right)=q\left(r_p,x,t\right)H\left(r_p,x,t\right)\int_0^\infty dr_s\left\{p\left(r_s,r_p\right)C\left(r_s,x,t\right)\right\} \tag{14}$$

In these equations, the value of $q(r_p,x,t)$ is expressed by Eq. (10). Thus, the integral terms (12), (13) are non-linear with regards to $H(r_p,x,t)$. Presence of the flux is important: it expresses the fact that the number of collisions between particles and pores is proportional to the particle flux.

2.1.5. Resulting System of Equations

The resulting system of equations is obtained by exclusion of the fine deposition $\partial\Sigma/\partial t$ from the balance equation (6) with its substitution from Eq. (9). It is also demonstrated in [37, 50] by volume balance considerations that the porosity and velocity may simultaneously be taken out of differentiation. The resulting system of equations for suspended particles and for pores assumes the form

$$\begin{aligned}&\phi\frac{\partial C\left(r_s,x,t\right)}{\partial t}+U\frac{\partial C\left(r_s,x,t\right)}{\partial x}=\\&-C\left(r_s,x,t\right)\frac{1}{L}\int_0^\infty p\left(r_s,r_p\right)q\left(r_p,x,t\right)H\left(r_p,x,t\right)dr_p;\end{aligned} \tag{15}$$

$$\begin{aligned}&\frac{\partial H\left(r_p,x,t\right)}{\partial t}=\\&\int_{r_p}^\infty dr_p^{'}\int_0^\infty dr_s\left\{p\left(r_s,r_p^{'}\to r_p\right)q\left(r_p,x,t\right)H\left(r_p,x,t\right)C\left(r_s,x,t\right)\right\}\\&-q\left(r_p,x,t\right)H\left(r_p,x,t\right)\int_0^\infty dr_s\left\{p\left(r_s,r_p\right)C\left(r_s,x,t\right)\right\}\end{aligned} \tag{16}$$

where $q(r_p,x,t)$ is given by Eq. (10).

Equations (15) and (16) form a system of non-linear integral-differential equations for the two functions: $C(r_s,x,t)$ and $H(r_p,x,t)$. Other values in this system are either known a priori or may be computed in terms of C and H. For example, in Eq. (15), velocity U may be treated either as constant or as a known function of time, due to incompressibility of the carrying liquid [39]. Porosity ϕ may be set constant for dilute suspensions. Otherwise, it may be computed in terms of $H(r_p,x,t)$. Considering porosity to be a free area per unit cross-section, we obtain:

$$\phi(x,t)=\int s(r_p)H(r_p,x,t)dr_p \tag{17}$$

where $s(r_p)$ is the cross-section of one capillary (for example, πr_p^2 for cylindrical capillaries).

System (15) and (16) requires one initial condition $H_0(r_p, x)$ for the pore concentration and one initial and one boundary condition for the particle concentration.

2.2. Averaging the System

The straightforward numerical solution of systems (15) and (16) is rather complicated. In order to study its physical implications, it is necessary to propose a method for the averaging (upscaling) of the system. Such a method was first proposed in [39] for a system of monodispersed particles (of the same size), with the size exclusion being the main capturing mechanism. In [50], in the framework of a different formalism, this method was generalized onto a polydisperse system. Here, we give a unified treatment of both cases, accounting for polydispersity of the particle ensemble and the possibility for incomplete plugging of the pores in the process of particle capturing.

2.2.1. The Monodisperse Case

For the case of filtration of the particles of the same size, distribution $C(r_s, x, t)$ is identical to the particle concentration $c(x,t)$ (more precisely, it is equal to $c(x,t)\delta(r_s - r_{s0})$). After some obvious transformations, systems (15) and (16) with the help of Eq.(10) are reduced to

$$\phi(x,t)\frac{\partial c(x,t)}{\partial t} + U\frac{\partial c(x,t)}{\partial x} = -\lambda(x,t)Uc(x,t); \tag{18}$$

$$\frac{\partial H(r_p,x,t)}{\partial t} = -A(r_p)c(x,t)U\frac{k_1(r_p)H(r_p,x,t)}{K(x,t)} \tag{19}$$

Here, the value $A(r_p)$, the filtration coefficient $\lambda(x,t)$ and permeability $K(x,t)$ are defined as

$$\lambda(x,t) = \frac{1}{L}\frac{\int_0^\infty p(r_p)k_1(r_p)H(r_p,x,t)dr_p}{K(x,t)},\ A(r_p) = p(r_p) - \int_{r_p}^\infty p(r_p' \to r_p)dr_p' \tag{20}$$

$$K(x,t) = \int_0^\infty k_1(r_p)H(r_p,x,t)dr_p \tag{21}$$

By $p(r_p)$, $p(r_p^{'} \to r_p)$ we denote, simply, the values of $p(r_s, r_p)$, $p(r_s, r_p^{'} \to r_p)$ for r_s equal to r_{s0}.

Eq. (18) represents the diffusion-free version of the classical equation (1), with variable porosity $\phi(x,t)$ and filtration coefficient $\lambda(x,t)$. These coefficients are defined in terms of the pore size distribution (cf. Eqs. (17), (20)). Therefore, the goal of up-scaling in this case is getting rid of the "distributed" equation (19), by reducing it to an equation similar to Eq. (2). This goal is achieved by the transformation of the independent variable $t : H(r_p, x, t) = H(r_p, x, h_o(x,t))$. Applying the chain rule,

$$\frac{\partial H\left(r_p, x, h_0\right)}{\partial h_0}\frac{\partial h_0}{\partial t} = -A(r_p)c(x,t)U\frac{k_1(r_p)H\left(r_p, x, h_0\right)}{\int_0^{\infty} k_1\left(r_p\right)H\left(r_p, x, h_0\right)dr_p} \tag{22}$$

We select variable h_0 in such a way that it includes all of the r_p-independent parts in the right-hand side of Eq.(22):

$$\frac{\partial h_0}{\partial t} = \frac{c(x,t)U}{\int_0^{\infty} k_1\left(r_p\right)H\left(r_p, x, h_0\right)dr_p} \tag{23}$$

It should be remarked that such a choice of the new independent variable is different from the choice in paper [39] where the described method for upscaling was originally developed. In that paper, it was proposed, simply, to select h_0 to be equal to the total concentration of pores $h(x,t)$. This choice is adequate for the case of size exclusion, where a captured particle totally closes a pore and excludes it from the flow. In this case, $h(x,t)$ is a decreasing function of time. However, in the case of incomplete plugging (where the pores are not excluded from the ensemble by the captured particles), the value of $h(x,t)$ remains invariable with time [37] and cannot be used as a new independent variable. For h_0, it is convenient to select $h_0(t=0) = 0$. Unlike $h(x,t)$, the value of h_0 has no clearly defined physical meaning.

With the definition (23), Eq. (22) is reduced to

$$\frac{\partial H\left(r_p, x, h_0\right)}{\partial h_0} = -A(r_p)k_1(r_p)H\left(r_p, x, h_0\right) \tag{24}$$

Its solution, with initial condition $H_0(r_p, x)$, is

$$H_0(r_p, x, h_0) = H_0(r_p, x)\exp\left(-A(r_p)k_1(r_p)h_0\right) \tag{25}$$

With the known function $H(r_p, x, h_0)$, the right-hand side of Eq. (23) becomes fully defined, and the equation assumes the form:

$$\frac{\partial h_0}{\partial t} = \frac{-c(x,t)U}{K(x,h_0)} \tag{26}$$

where the denominator $K(x,h_0) = \int_0^\infty k_1\left(r_p\right)H\left(r_p, x, h_0\right)dr_p$ is permeability (21) with the time variable substituted by h_0. Moreover, with the known dependence $H_0(r_p, x, h_0)$, the values of porosity ϕ and filtration coefficient λ also become the known functions of x, h_0 (cf. equations (17), (20)). Correspondingly, the mass balance equation is reduced to

$$\phi(x,h_0)\frac{\partial c\left(x,t\right)}{\partial t} + U\frac{\partial c\left(x,t\right)}{\partial x} = -\lambda(x,h_0)Uc(x,t); \tag{27}$$

Equations (26), (27) form the complete upscaled system of the two equations for functions $c(x,t), h_0(x,t)$, from which the pore size distribution is excluded. The evolution pore size distribution may be found from Eq. (25) after solution of this system. System (26), (27) takes into account evolution of the porosity and filtration coefficient due to pore plugging.

2.2.2. The Polydisperse Case

The derivation of the previous subsection may be generalized onto the polydisperse case. Assume that the particles may possess n distinct sizes $r_{s1}, ..., r_{sn}$, and denote by $c_i(x,t)$ the concentration of the particles of the size r_{si}. Then the particle size distribution is represented in the form

$$C(r_s, x, t) = \sum_i c_i(x,t)\delta(r_s - r_{si}) \tag{28}$$

The equation for $C(r_s, x, t)$ is disintegrated into n equations

$$\phi(x,t)\frac{\partial c_i\left(x,t\right)}{\partial t} + U\frac{\partial c_i\left(x,t\right)}{\partial x} = -\lambda_i(x,t)Uc_i(x,t)\ (i = 1, ..., n) \tag{29}$$

Equation for $H(r_p, x, t)$, after some transformations, assumes the form of

$$\frac{\partial H\left(r_p, x, t\right)}{\partial t} = -\sum_i c_i(x,t) A_i(r_p) U \frac{k_1(r_p) H\left(r_p, x, t\right)}{K(x,t)} \tag{30}$$

In the last two equations, the coefficients are defined similarly to the previous subsection:

$$\begin{aligned} \lambda_i(x,t) &= \frac{1}{L} \frac{\int_0^\infty p_i\left(r_p\right) k_1(r_p) H\left(r_p, x, t\right) dr_p}{K(x,t)}; \\ A_i(r_p) &= p_i(r_p) - \int_{r_p}^\infty dr_p' \left\{ p_i\left(r_p' \to r_p\right) \right\} \end{aligned} \tag{31}$$

Permeability $K(x,t)$ is defined in Eq. (21). By $p_i(r_p)$, $p_i(r_p' \to r_p)$ we denote $p(r_{si}, r_p)$, $p(r_{si}, r_p' \to r_p)$, correspondingly.

Generalizing the results of the previous subsection, we search solution $H(r_p, x, t)$ of Eq. (30) in the form of $H(r_p, x, h_1, ..., h_n)$. The unknown functions $h_i(x,t)$ are set to obey the equations similar to Eq. (23):

$$\frac{\partial h_i}{\partial t} = -\frac{c_i(x,t) U}{\int_0^\infty k_1\left(r_p\right) H\left(r_p, x, t\right) dr_p} \tag{32}$$

This is possible if (according to the chain rule applied to Eq. (30)) function $H(r_p, x, h_1, ..., h_n)$ obeys the series of equations

$$\frac{\partial H\left(r_p, x, h_1, ..., h_n\right)}{\partial h_i} = -A_i(r_p) k_1(r_p) H \quad (i = 1, ..., n) \tag{33}$$

These equations are compatible, since $\partial^2 H / \partial h_i \partial h_j = \partial^2 H / \partial h_j \partial h_i$. Their solution has the form similar to Eq. (25). Taking into account initial conditions $h_i(t=0) = 0$,

$$H\left(r_p, x, h_1, ..., h_n\right) = H_0(r_p, x) \exp\left(-\sum_i A_i(r_p) k_1(r_p) h_i \right) \tag{34}$$

Substituting this dependence into system (29), (32) reduces it to the system of $2n$ equations for variables $c_i(x,t), h_i(x,t)\ (i = 1, ..., n)$:

$$\phi(x,h_1,...,h_n)\frac{\partial c_i(x,t)}{\partial t}+U\frac{\partial c_i(x,t)}{\partial x}=-\lambda_i(x,h_1,...,h_n)Uc_i(x,t); \tag{35}$$

$$\frac{\partial h_i}{\partial t}=-\frac{c_i(x,t)U}{K(x,h_1,...h_n)}\ (i=1,...,n) \tag{36}$$

Here, porosity ϕ, permeability K and filtration coefficients λ_i are calculated as (cf. Eqs.(17), (20), (21))

$$\phi(x,h_1,...,h_n)=\int_0^\infty s\left(r_p\right)H_0(r_p,x)\exp\left(-\sum_i A_i(r_p)k_1(r_p)h_i\right)dr_p; \tag{37}$$

$$K(x,h_1,...,h_n)=\int_0^\infty k_1\left(r_p\right)H_0(r_p,x)\exp\left(-\sum_i A_i(r_p)k_1(r_p)h_i\right)dr_p; \tag{38}$$

$$\lambda_i(x,h_1,...,h_n)=\frac{1}{l}\frac{\int_0^\infty p_i\left(r_p\right)k_1(r_p)H_0(r_p,x)\exp\left(-\sum_i A_i(r_p)k_1(r_p)h_i\right)dr_p}{K(x,h_1,...,h_n)} \tag{39}$$

2.2.3. Discussion

We have shown that for a particle ensemble with *n* distinct particle sizes, the system of non-linear integral-differential equations (15) and (16) may be reduced to the system of n linear hyperbolic equations (35) coupled with n differential equations (36). This is a definite simplification of the governing equations, making their analysis and numerical solution more convenient. It should be stressed that the simplification may only be achieved with regard to the pore size distribution. Polydispersity of the particle system, seemingly, cannot be averaged without very strong assumptions. The particles of the different sizes are filtered in the different ways, and the system with n different particle sizes requires, at least, n distinct transport equations.

For a monodisperse system, only one hyperbolic transport equation (27) is required, coupled with one differential equation (26). The transport equation (27) is similar to the classical equation (1), apart from the diffusion term present in the latter equation. Diffusion might be taken into account by direct introduction into the "distributed" governing equation (15). To the best of our knowledge, this has not been done yet.

A gain of the ensemble-based treatment of the monodisperse particle system, compared to the classical treatment, is an explicit expression for the evolution of the pore size distribution, and the corresponding expressions for evolution of porosity, permeability and filtration coefficient. These expressions are more theoretically grounded than multiple empirical correlations suggested in the literature (see, for example, [3, 62-64]).

The same gain is achieved for polydisperse systems. Evolution of permeability, porosity, and filtration coefficients for the different kinds of particles are expressed in terms of the auxiliary functions $h_1,...,h_n$. The system of equations for these functions and for the concentrations is coupled, which reflects the fact that the particles of different kinds compete for the porous space and for the deposition sites. This competition would be difficult to describe adequately in the framework of the classical formalism.

3. CTRW Approach

3.1. Introduction

In this section, we review the basics of the continuous time random walks (CRTW) approach, as applied to filtration. The CTRW approach to modeling tracer and suspension flows in porous media incorporates the effects of small-scale median heterogeneity by applying the distribution of particle flights and residence times. The model is validated by the comparison between modeling results and the experiments with artificially created median heterogeneity.

An excellent recent review of the application of the theory to tracer propagation in porous media was presented in [40], and there is no reason to repeat it here in detail. We only overview some basic statements of the theory regarding the tracer flows and show their extension onto the filtration (equivalent to transport of tracers with possible precipitation/adsorption). We also compare the CTRW to other approaches.

The CTRW approach, as many other developments in stochastic processes, has started from the famous works of Einstein, Langevin and Smoluchowski about Brownian motion of the particles [19, 54, 65, 66] (see extensive discussion in Ref. [67]). The original equation, from which Einstein derives the Fick-like theory of Brownian motion, has the form of

$$c(x,t) = \int c(x-l, t-\tau)\psi(l)dl \tag{40}$$

Here, $\psi(l)$ is the distribution density for displacement of a Brownian particle during time τ, which Einstein considers to be fixed. Expanding the equation in an assumption about finiteness of the second moment of the symmetrical distribution $\psi(l)$, Einstein recovers the Fick diffusion equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}, D = \frac{\left\langle l^2 \right\rangle}{2\tau} \tag{41}$$

The first generalization introduced by the CTRW into the scheme above, are the assumption about the random distribution of time τ of the particle flight. That is, the CTRW assumes that the time intervals during which a particle performs *independent* displacements may be distributed. This assumption leads to non-trivial consequences: for example, it is demonstrated in [44] by direct numerical experiments that the concentration profiles for a

particle ensemble where both jump times and steps are distributed may differ from the Gaussian profile $\exp\left[-x^2/4Dt\right]/2\sqrt{\pi Dt}$ predicted by the classical diffusion theory.

Another generalization, which distinguishes the CTRW from the original Einstein scheme, is refusal from finiteness of the second moments of the distribution $\psi(l)$. Moreover, the distribution of time τ may also possess infinite moments. This results in unusual asymptotic behavior of concentration $c(x,t)$, which is not described by the consequences of the Central Limit Theorem. The theory of Levy flights and fractional differential equations [68-73] has been developed for such types of processes. They are not considered here.

3.2. Basic Relations

Consider the motion of the tracer particles in an infinite one-dimensional region. Generalization from tracers onto filtration will be considered later in Section 3.4. The particles move independently, starting from initial position $x=0$. We will approximate real continuous motion of the particles by a series of discrete steps: a particle stays at a position x during a random time τ, and then jumps instantaneously into another position x'. This approximation is reasonable for a series of multiple small flights. The transition distribution $\psi(x_1 \to x_2, \tau)$ is the main characteristics of the particle motion. This function is defined as a probability that a particle jumps from point x_1 to x_2 during time τ. For the tracer flow, this probability normed to unity:

$$\int \psi(x_1 \to x_2, \tau) dx_2 d\tau = 1$$

The fact that $\psi(x_1 \to x_2, \tau)$ depends on x_1 (that is, that jumps from the different points are unequally distributed) makes it possible to account for heterogeneity of the medium (e.g. ground) where the flow occurs. In a homogeneous medium, ψ depends on $x_2 - x_1$ (see discussion below).

Consider distribution $R_n(x,t)$ of the positions of the particles right after nth jump. Distributions R_n are expressed in terms of each other by the recurrent relation

$$R_n(x,t) = \int \psi(x' \to x, t-t') R_{n-1}(x',t') dx' dt'$$

If all of the particles start from the origin, then

$$R_0(x,t) = \delta(x)\delta(t-0^+)$$

Distribution of all of the particles, independently of the number of jumps, is

$$R(x,t)=\sum_{i=0}^{\infty}R_i(x,t)$$

Applying operator $\int\psi(x',t-t'\,|\,x)\circ dx'dt'$ to the last sum, we obtain equation

$$R(x,t)-\int\psi(x'\to x,t-t')R(x',t')dx'dt'=\delta(x)\delta(t-0^{+}) \tag{42}$$

The case where not all of the particles start from the origin is obtained by substituting an arbitrary initial distribution $R_0(x)$ instead of $\delta(x)$ into the right-hand side of the last equation. Anyway, this right-hand side is equal to zero anywhere at $t>0$.

Eq. (42) is similar to Einstein's equation (40), apart from the fact that the time of flights is also distributed. The particle number concentration $c(x,t)$ consists of all of the particles that have come to point x earlier and stayed there until now:

$$c(x,t)=\int\Psi(t-t'\,|\,x)R(x,t')dt';\ \Psi(\tau\,|\,x)=1-\int_0^{\tau}\psi(t'\,|\,x)dt' \tag{43}$$

Here, for brevity, we denote by $\psi(\tau\,|\,x)$ the partial density $\int\psi(x\to x',\tau)dx'$. The difference between $c(x,t)$ and $R(x,t)$ becomes negligible for small and reasonably bounded time steps. For example, in the original Einstein scheme, it is not taken into account. However, if the moments of the time step becomes infinite and/or it possesses a power law-distributed "tail", this correction becomes important.

Another form of the equation for the concentration, which is used in the CTRW approach, is

$$\frac{\partial c}{\partial t}=-\int w(x',x,t-t')c(x,t')dx'dt'+\int w(x,x',t-t')c(x',t')dx'dt' \tag{44}$$

Function $w(x',x,\tau)$ is generally different from the transition distribution $\psi(x\to x',\tau)$ (and, even, has a different dimension). The relation between them is established in the next subsection. Function $w(x',x,\tau)$ expresses the frequency of transition from point x' to point x. Correspondingly, the first term in Eq. (44) expresses the frequency of leaving point x, while the second term expresses the frequency of coming to this point. The choice between system (42)-(43) and Eq. (44) depends on convenience for a particular problem.

The two simplifications are often introduced, separately or together:

1) *Homogeneous medium*. In this case, the jumps from each point have similar distributions. Correspondingly, both the transition distribution $\psi(x\to x',\tau)$ and the transition frequency $w(x',x,\tau)$ depend on the difference $x-x'$:

$$w(x',x,\tau) = w(x'-x,\tau);\ \psi(x \to x',\tau) = \psi(x-x',\tau) \tag{45}$$

(In order to not get lost in the designations, we use the same letters for the functions of the different numbers of the arguments, provided that these functions have the same meaning. The difference is indicated by an explicit list of the arguments.)

2) *Stationary process*. The process is called stationary if its transition probabilities/frequencies are independent of time [20]. It should be remarked that a process may be stationary, while its trajectories develop in time. For example, the standard Brownian motion is a stationary process. The motion of tracer or filtration of suspension may often be considered to be stationary if it does not modify the properties of the carrying medium.

With regard to CTRW, this means that the transition frequencies $w(x',x,\tau)$ become independent of τ (more precisely, and with some ambiguity in designations, $w(x,x',\tau) = w(x,x')\delta(\tau)$). Correspondingly, Eq. (44) is simplified to

$$\frac{\partial c}{\partial t} = -\int w(x',x)c(x,t)dx' + \int w(x,x')c(x',t)dx' \tag{46}$$

The form of distribution ψ corresponding to the stationary process is more complicated. It will be derived in the next subsection.

3.3. Laplace Transform

Eqs. (42), (43), (44) contain convolutions and derivatives with regard to time. It is natural to study them by means of the Laplace transform. Let u be the Laplace transformed variable t. We denote Laplace transforms of the functions by the same letters as functions themselves, indicating the transformation by substituting the argument t by u. Eqs. (42), (43) are then transformed to

$$R(x,u) - \int \psi(x' \to x,u)R(x',u)dx' = \delta(x); \tag{47}$$

$$c(x,u) = \frac{1-\psi(u \mid x)}{u} R(x,u) \tag{48}$$

Eq. (44) is transformed to

$$uc = -\int w(x',x,u)c(x,u)dx' + \int w(x,x',u)c(x',u)dx' \tag{49}$$

It is possible now to express the Laplace transform $w(x',x,u)$ of the frequency of jumps in terms of the transformed jump distribution $\psi(x' \to x \mid u)$. Expressing $R(x,u)$ in terms of $c(x,u)$ from Eq. (48) and its substitution to Eq. (47) results, after some obvious algebraic transformations, in

$$uc(x,u)-\delta(x)=-\frac{uc(x,u)\int\psi(x\to x',u)dx'}{1-\psi(u\mid x)}+\int\frac{u\psi(x'\to x,u)}{1-\psi(u\mid x)}c(x',u)dx'$$

Comparison to Eq. (49) results in the following expression for w :

$$w(x',x,u)=\frac{u\psi(x\to x',u\mid x)}{1-\psi(u\mid x)} \tag{50}$$

The last relation shows that the two approaches to CTRW based on system (42), (43), and based on Eq. (44) are equivalent.

Eq. (50) may be inverted, so that $\psi(x\to x',u)$ becomes expressed in terms of $w(x',x,u)$. The first task is to find $\psi(u\mid x)$. Integrating Eq. (50) over x', we obtain:

$$\int w(x',x,u)dx'=\frac{u\psi(u\mid x)}{1-\psi(u\mid x)},\ \text{Or}\ \psi(u\mid x)=\frac{\int w(x'',x,u)dx''}{u+\int w(x'',x,u)dx''}$$

Substitution of the last relation back into Eq. (50) and expressing $\psi(x',u\mid x)$ results in

$$\psi(x\to x',u)=\frac{w(x',x,u)}{u+\int w(x'',x,u)dx''}$$

This is the expression for the transition distribution in terms of the transition frequency in Laplace transforms. The inverse Laplace transform may be found for an important particular case of a stationary CTRW process (see the definition in the previous subsection). For this case, w is independent of u ; hence, expression for ψ has the form of $a/(u+b)$, where a and b are independent of u . Correspondingly, inversion of the Laplace transform results in

$$\psi(x\to x',\tau)=w(x',x)\exp\left[-\tau\int w(x'',x)dx''\right]$$

This is an expression for the transition distribution density for a stationary process that was announced in the previous subsection.

3.4. Extension onto Filtration

So far, we have described motion of the tracer particles, which do not “disappear” in the course of their motion. On the contrary, in the process of filtration, some particles may deposit and become excluded from the flow. One way is to express it mathematically by introducing probability $p(x)$ that a particle is caught in the course of one flight. In other

words, not all of the particles arrive to point x after a flight, since part $p(x)$ of them disappears from the flow. Equation (42) in this case assumes the form of

$$R(x,t)-(1-p(x))\int\psi(x'\to x,t-t')R(x',t')dx'dt'=\delta(x)\delta(t-0^+) \qquad (51)$$

Eq. (43) relating concentration to function $R(x,t)$ remains valid. Moreover, the computations from previous subsection may be repeated with only minor changes. All of the relations between functions ψ and w remain the same, while Eq. (44) is transformed to

$$\frac{\partial c}{\partial t}=-\int w(x',x,t-t')c(x,t')dx'dt'+(1-p)\int w(x,x',t-t')c(x',t')dx'dt' \qquad (52)$$

That is, for the case of irreversible deposition, more particles, on average, leave any point x than come to this point.

Another way to account for particle deposition was proposed in [74] and further developed in [75]. In this approach, the particles are assumed to be deposited in the "traps", where they spend indefinite time and then may return to the flow. The distribution $Z(\tau\,|\,T)$, of time τ, which a particle spends in the traps while flying time T, is assumed to be known. For example, if the time distribution for a single trap is $\zeta(\tau)$, and the traps appear independently with frequency λ, then $Z(\tau\,|\,T)$ is described by the generalized Poissonean process [20]:

$$Z(\tau\,|\,T)=e^{-\lambda T}\delta(t-0^+)+\sum_{k=1}^{\infty}\frac{(\lambda T)^k}{k!}e^{-\lambda T}[\zeta^*]^k$$

Here, designation $*$ is used for the operation of convolution with regard to time.

In a homogeneous medium, distribution $\psi(x,t)$ of the distance and time of flight for a particle that may deposit, is obtained on the basis of a hypothetical distribution $\psi_0(x,t)$ of the flight of a particle without deposition:

$$\psi(x,t)=\int\psi_0(x,t-\tau)Z(\tau\,|\,T-\tau)d\tau \qquad (53)$$

In such a way it is taken into account that trapping during longer flights is more probable than trapping during shorter ones, and that a particle may stay in the traps for a longer time during longer flights. An alternative formalism based on the distribution $Z(\tau\,|\,x)$ of the trapping times depending on the distance rather than on the time of flight may also be developed.

A ready function $\psi(x,t)$ given by Eq. (53) serves as the basis for the same formalism as developed above, so that Eqs. (42), (43), (44) and their consequences remain valid. It should

be noticed that in this formalism, $c(x,t)$ becomes the total concentration of the particles (both flowing and deposited). The concentration of free (suspended) particles is denoted by $g(x,t)$, while their difference $s(x,t)$ is the amount of the deposited particles. For the last amount, the authors [74] obtain the equation with memory:

$$\frac{\partial s(x,t)}{\partial t} = \lambda g(x,t) - \lambda \int_0^t \zeta(t-\tau) g(x,\tau) d\tau$$

The formalism described in [74] seems to be more appropriate for reversible particle deposition. The irreversible deposition may to some extent be modeled by very long characteristic times τ. However, such a formal approach may create problems with boundary conditions and with a numerical solution of the equations with memory. In our opinion, the approach based on Eqs. (51), (52) is more appropriate for irreversible deposition, while the approach suggested in [74] is suitable for reversible sorption.

The two important problems, to the best of our knowledge, have not been considered in the framework of the discussed formalism. The first problem is filtration of an ensemble of distributed particles, similar to that considered in Section 2. If the suspension is dilute, and the particles of the different sizes flow independently from each other, generalization of the theory above onto the different particles becomes almost trivial. However, if the particles in the ensemble interact with each other and "compete" for the porous space, the generalization becomes difficult.

Another non-trivial generalization is required for the case where the deposited particles plug the porous medium, changing its properties. Such changes have been described in the framework of the population balance approach; however, they are rather difficult to model in the framework of the "straightforward" CTRW approach.

Below we will show how these two problems have been resolved in the version of the CTRW based on the elliptic transport equation.

3.5. Solution of the Equations

Solution of any system of transport equations requires initial and boundary conditions. The theory developed above exceeds from an ensemble of particles, which in initial moment $t = 0$ is concentrated at one point $x = 0$. The particles move in an infinite region $-\infty < x < \infty$.

Since the transport equations are linear with regard to particle concentration, they remain valid for arbitrary initial distribution $c_0(x)$. Such a distribution should be substituted instead of $\delta(x)$ into Eq. (42) or be used as an initial condition for Eq. (44), or their generalizations (51), (52).

The problems arise when transport in a bounded region is considered. An integral-differential equation like (44) would require a boundary condition given at a certain interval. It is not clear in advance how to formulate such a physically grounded condition. Similar and even larger problems may arise when the formalism is generalized onto multiple dimensions. To the best of our knowledge, these problems have not been considered in the literature.

It has been shown in a number of Refs [26, 27, 40, 41, 43, 49, 76] that the CTRW transport equations can be formulated in Laplace space, to represent the time derivative in an algebraic expression [27, 40, 41, 49, 76]. This is a natural consequence of the fact, that the time integrals in Eqs. (42), (43), (44) are of the convolution type, which is transformed to a product by the Laplace transform. If the medium, where transport occurs, is homogeneous, then the integrals over the spatial variable also become of the convolution type (cf. Eq. (45)). Then the Fourier transform with regard to x is applied additional to the Laplace transform with regard to t, reducing Eqs. (42), (44) to algebraic equations, from which the unknown functions may easily be expressed. Inverse transforms are often difficult to be taken analytically, or result in analytical solutions expressed in complex hypergeometric functions [77, 78]. However, they may be used in order to analyze the asymptotics of the obtained solutions on the basis of the Tauberian theorems [20] or similar statements (see examples in [79]).

A particular interesting case of transport in a homogeneous medium is analyzed in [26], where the times of flight are assumed to be uncorrelated with the flight distances. Then the expression for $\psi(x'-x,t)$ may be represented as a product of the two kernels depending of x and t, correspondingly. As follows from Eq. (50), expression for $w(x'-x,t)$ may also be factorized:

$$\psi(x'-x,t) = m(t)d(x'-x);\ \ w(x'-x,t) = M(t)d(x'-x) \tag{54}$$

where, in Laplace images,

$$M(u) = \frac{um(u)}{1-\psi(u)}$$

For such cases, it is proven in [26] that the Laplace-transformed solution $c(x,u)$ of Eq. (44) is obtained from solution $c_1(x,u)$ of the same equation, but with $M(u)=1$:

$$c(x,u) = c_1\left(x, \frac{u}{M(u)}\right) \tag{55}$$

Further analysis may be carried out under conditions (54) for small displacements $x'-x$. Expansion of Eq. (44) up to the second-order terms with regard to $x-x'$ results in the ADE equation (1) (without the deposition term) corrected for the memory function:

$$\frac{\partial c}{\partial t} = M(t) * \left[-v\frac{\partial c}{\partial x} + D\frac{\partial^2 c}{\partial x^2} \right]$$

Such an equation is analogous, although not fully similar to the elliptic formalism considered below. Its solution may be obtained from the solution c_1 of the "standard" ADE with the help of substitution (55).

3.6. Verification with Experiments

Comparison of the CTRW theory with the experiments has been mostly carried out for the tracer flows [26, 27, 40-42, 49, 80]. To the best of our knowledge, the only work where the theory was compared with the experimental data involving deposition of the flowing particles (or bacteria) is [75]. Qualitative observations show that the CTRW is able to explain and describe the three important effects that were observed in experiments [26, 27, 75] and in the nature [40, 42, 49], but cannot be adequately described by the ADE: 1) Under pulse injection, the maximum of the concentration moves slower than the flow rate of the carrying fluid; 2) The concentration distribution around the maximum is asymmetric, and 3) There is a forward "tail" of the concentration, which contains much more particles and decreases much slower than predicted by the ADE (Figure 2). For the case of filtration, the distributed particle flights described by the CTRW may contribute to non-exponential deposition profiles [11, 46, 50], although this contribution may be less significant than the contribution of the particle size distributions.

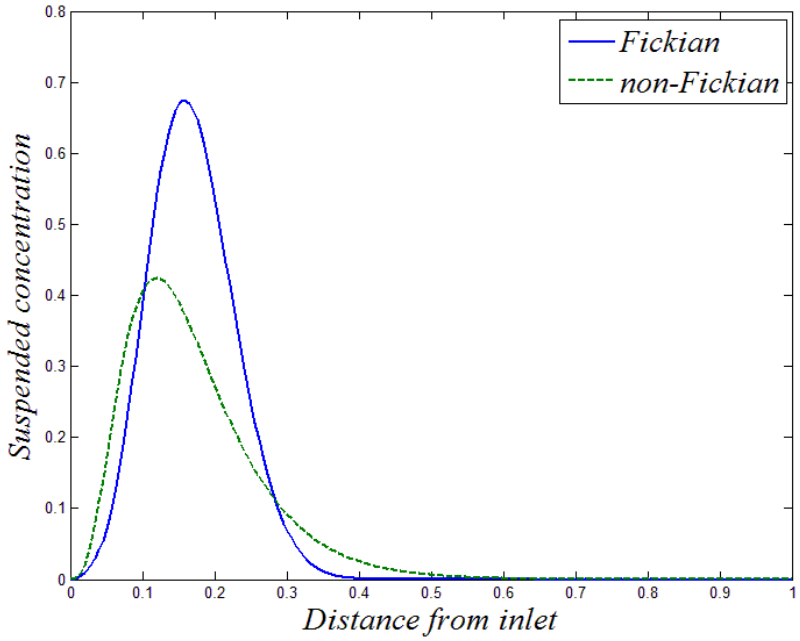

Figure 2. Distribution of suspended concentration at a certain time in a pulse-injection case.

Since the CTRW approach is designed to account for small-scale median heterogeneity, the degree of heterogeneity of the porous media adopted for filtration experiments requires careful selection. It has been shown in a number of works [26, 27, 40-42, 49, 80] that the CTRW approach is able to catch the non-Fickian behavior of particles in various types of heterogeneous porous media. The scale of median heterogeneity may also vary from pore scale to small scale (several centimeters). An artificially heterogeneous porous medium used in experiments may contain heterogeneities following the different patterns (ordered or stochastically correlated). This may affect the experimental results [26, 28].

The ability of the CTRW approach to catch anomalous transport in heterogeneous porous media has been well-proved in the above mentioned works. Nevertheless, uniqueness of the model parameter estimation on the basis of experimental data and the predictive capability of the theory are two factors to evaluate the practical performance of a model. It has been shown in Ref. [46] that the CTRW approach can match a non-Fickian breakthrough curve, while the 95% confidence intervals of model parameter estimation are relatively large. Correlations were also observed between the different parameters of the model. This indicates that the CTRW approach may be over-parameterized from the practical point of view. The parameter estimation method by fitting breakthrough curves seems to be insufficient.

4. The Elliptic Equation Approach

It has been shown that under certain conditions the CTRW description of tracer and particle flow may be reduced into an elliptic partial differential equation in the limit of infinitely many infinitesimal step lengths and residence times [44]. Such an equation produces more dispersed breakthrough curves with the early arrival and the delay of particles compared to the Fickian approach based on Eqs. (1), (2). The resulting deposition profiles are hyper-exponential. Thus, the elliptic equation (EE) approach retains the essential features of the CTRW approach, strongly reducing its complexity. This has made it possible to generalize the EE approach onto multi-disperse systems interacting with porous media [50].

In this section, the basic derivations and the principles of elliptic equation approach are introduced.

4.1. Monodisperse Systems

Let us consider the transport equation (42) and apply to both its sides operator $\Psi(t \mid x)*$, where the convolution is taken by time t and function Ψ is defined in Eq. (43). Since convolutions are interchangeable, and in view of the Eq. (43), Eq. (42) is transformed to

$$c(x,t) - \int \psi(x, x-x', t-t')c(x',t')dx'dt' = \delta(x)\Psi(t)$$

Here, we represented kernel $\psi(x' \to x, t-t')$ as a function of variables x and $x-x'$. Such a representation may be advantageous, since the scale of heterogeneity variation, reflected by argument x, may usually be much larger than the particle flight $x-x'$. Renaming the arguments in the convolution, we obtain:

$$c(x,t) - \int \psi(x,l,\tau)c(x-l,t-\tau)dld\tau = \delta(x)\Psi(t) \tag{56}$$

This equation is similar to the Einstein equation (40), apart from the fact that the time step in it is also distributed. The right-hand side in it is localized by space and time (at least, for reasonably bounded distributions $\psi(\tau \mid x)$ and may usually be neglected.

Straightforward expansion of $c(x-l,t-\tau)$ in Eq. (56) up to the second order terms results in:

$$\frac{\partial c}{\partial t}+\frac{\partial c}{\partial x}=D_x\frac{\partial^2 c}{\partial x^2}+D_t\frac{\partial^2 c}{\partial t^2}+D_{xt}\frac{\partial^2 c}{\partial x\partial t}; \tag{57}$$

Here,

$$v=\frac{\langle l\rangle}{\langle\tau\rangle};\ D_x=\frac{\langle l^2\rangle}{2\langle\tau\rangle};\ D_t=\frac{\langle\tau^2\rangle}{2\langle\tau\rangle};\ D_{xt}=\frac{\langle l\tau\rangle}{\langle\tau\rangle}; \tag{58}$$

$$\langle l^n\tau^m\rangle=\int l^n\tau^m\psi(x,l,\tau)dld\tau$$

A similar expansion of the filtration equation (51) is also possible. Similar to considerations above, we obtain:

$$\frac{\partial c}{\partial t}+\frac{\partial c}{\partial x}=D_x\frac{\partial^2 c}{\partial x^2}+D_t\frac{\partial^2 c}{\partial t^2}+D_{xt}\frac{\partial^2 c}{\partial x\partial t}-\Lambda c; \tag{59}$$

$$\Lambda=\frac{p(x)}{(1-p(x))\langle\tau\rangle} \tag{60}$$

Other coefficients apart Λ are defined similarly in Eqs. (57), (59).

A weak point in the derivation above is the Taylor expansion: one may ask, in principle, why we terminate the expansion exactly at the second-order terms? Fundamental reasons for that, apart from historical tradition starting from Fick and Einstein, are discussed in [44, 45, 50]. They may be outlined as follows. For simplicity of discussion, let us consider the case of transport of a tracer in a homogeneous medium, where the transition probability $\psi(x,l,\tau)$ is independent of x. In this case, sequence $\{R_n(x,t),\ n=1,...,\infty\}$, introduced in Section 3.2, forms a discrete stochastic semigroup with regard to operation of convolution by x,t:

$$R_n * R_m = R_{n+m}$$

We would like to consider the limiting behavior of this semigroup when the flights tend to zero, but their number to infinity. In this limit, the stochastic semigroup $\{R_n\}$ is turned into a continuous semigroup representing the continuous stochastic process R_z. It is physically reasonable to assume that R_z represents the process with continuous trajectories. It has been proven [20] that an infinitesimal operator for such a process is a second-order differential operator:

$$\frac{\partial R_z}{\partial z}+\frac{\partial R_z}{\partial t}+\frac{\partial R_z}{\partial x}=D_x\frac{\partial^2 R_z}{\partial x^2}+D_t\frac{\partial^2 R_z}{\partial t^2}+D_{xt}\frac{\partial^2 R_z}{\partial x\partial t}$$

The higher-order terms in the expansion disappear for the processes with continuous trajectories, while the governing equation for the processes with discontinuities should contain integral terms. Concentration $c(x,t)$ is represented by the sum $\sum R_n$, which, in the limit of many infinitely small steps, becomes the resolvent integral $\int_0^\infty R_z dz$. Thus, integrating the last equation over z, we obtain Eq. (57).

Considerations above show that, in order to achieve convergence, the coefficients given by Eq. (58) should tend to finite limits. This is common for Markov processes with continuous trajectories. Equation (60) introduces additional assumption, that $\Lambda = p/\langle\tau\rangle$ should tend to a constant limit as $\langle\tau\rangle \to 0$ and, in particular, $p \to 0$ in this limit. It is rather straightforward to generalize the semigroup-based theoretical considerations above onto this case. A more complex generalization considered in [45] is when the capturing probability is also the distributed value and may vary for the same flight times and distances.

The value of Λ has a meaning of the probability of capturing per unit time of the particle flight. In the filtration theory, the filtration coefficient probability of capturing per unit length of flight $\lambda = p/\langle l\rangle$ is often introduced. It is easy to see from Eq. (58) that $\Lambda = v\lambda$.

In the limit of many infinitely small steps, such values as $\langle l\rangle, \langle\tau\rangle$ and other moments of the flights during one step tend to zero. In practical applications, it is more convenient to consider them to be small, but finite values. This is the assumption exploited in further developments. Tending to the limit is only needed in order to substantiate the selected form of the governing equations.

4.2. Polydisperse Systems

4.2.1. Introduction. Dilute Suspensions

As in Section 2, consider the suspension of the particles distributed by sizes r_s. As discussed in Section 2.1.1, such a suspension is characterized by the distributed concentration of particles $C(r_s,x,t)$. As a first approach to the problem, consider the case of a diluted suspension, where all of the particles flow independently and do not "spoil" the porous medium. Then, Eq. (59) may be applied to the particles of each size separately:

$$\frac{\partial C}{\partial t}+v\frac{\partial C}{\partial x}=D_x\frac{\partial^2 C}{\partial x^2}+D_{xt}\frac{\partial^2 C}{\partial x\partial t}+D_t\frac{\partial^2 C}{\partial t^2}-\Lambda C(r_s,x,t) \tag{61}$$

Since the particles of the different sizes may move, be dispersed, and deposit with the different rates, the coefficients in this equation depend on size r_s. The character of this dependence should be established on the basis of the known mechanisms of the particle-pore interactions. Thus, even for dilute suspensions, consideration of the interactions of the ensembles of particles and pores should be the part of a model.

Consideration of ensembles of particles in pores in the framework of the CTRW/elliptic formalism is much more elaborate. It will be described below, following work [50], with some simplifications.

4.2.2. Particle Flow Characteristics

Apart from concentration $C(r_s,x,t)$, we have to introduce a distributed pore concentration, similar to Section 2.1.1. This distribution, $H(l,r_p,x,t)$, will be different from the distribution $H(r_p,x,t)$ used in the section about population balance, in the two important points. First, unlike Section 2, distribution $H(l,r_p,x,t)$ is defined to be per unit volume, but not per unit cross-section. Secondly, in order to account for the travel distances of the particles, we do not consider the pore distribution only by sizes r_p, but also by travel distances l. The values of l should not be abstract "sizes", as in Section 2, but real distances or, rather, their projections on axis x. Due to the plugging of the porous medium, distribution H may vary with time and in space, and this variation requires a special equation.

In order to simplify the discussion compared to the general and cumbersome formalism considered in [50], we assume that the capturing of the particles is a purely geometric event and depends only on the particle size r_s and pore sizes l,r_p. Thus, we may define the a priori passing probability $P(r_s,l,r_p)$ that a particle of a size r_s is NOT captured in a pore of sizes l,r_p. Then, a priori probability for a particle to be captured is $p(r_s,l,r_p)=1-P(r_s,l,r_p)$. Many studies indicate that the particle capture may also be rate-dependent [1-3, 81]. Such cases require a separate study in the framework of a more general concept [50].

It should be remarked that probability $P(r_s,l,r_p)$ is determined "per pore". The a posteriori passing probability, or the probability $P(r_s,x,t)$ to pass a given point in a given time moment, will be defined in the next section.

Another a priori characteristic necessary for the model is the distribution of particle flight times $\psi(\tau\,|\,r_s,l,r_p,x,t)$. As usual, in the probability theory, we use designations like $g(A\,|\,B)$ to denote the distribution of the set of variables A under conditions (fixed variables) B. The functional form $\psi(\tau\,|\,r_s,l,r_p,x,t)$ indicates that we assume the flight times to be dependent of all of the other parameters of a particle and a pore. The conditional distribution may depend on x and t since the residence times of particles in pores depend on hydrodynamic velocities. As a general measure of the local velocity field, the macroscopic hydrodynamic velocity U/ϕ may be selected. Then it is reasonable to assume that [50]

$$\psi(\tau \mid r_s, l, r_p, x, t) = \psi_U(\phi l / U\tau \mid r_s, l, r_p)\frac{\phi l}{U\tau^2} \tag{62}$$

On the basis of the introduced distributions and probabilities, the expressions for other distributions may be derived. For example, the distribution transition function similar to function $\psi(l,\tau)$ used in the CTRW approach has the form of

$$\psi(l, \tau \mid r_s, r_p, x, t) = \psi(\tau \mid r_s, r_p, x, t) f(l, r_p, x, t) \tag{63}$$

Here, $f(l, r_p, x, t)$ is the pore distribution function, which is defined on the basis of $H(l, r_p, x, t)$ similarly to Section 2.1.1:

$$h(x,t) = \int H\left(l, r_p, x, t\right) dr_p; \;\; f\left(l, r_p, x, t\right) = \frac{H\left(l, r_p, x, t\right)}{h(x,t)}$$

Unlike the previous cases, the flight distribution depends $\psi(l, \tau \mid r_s, r_p, x, t)$ on the local pore size distribution and may vary with time.

4.2.3. Basic Equations

The basic equation for particle size distribution $C(r_s, x, t)$ retains the form (61) and is derived in a similar way to the monodisperse case [50]. The coefficients in it are defined as

$$v = \frac{L(r_s, x, t)}{T(r_s, x, t)}; \;\; D_x = \frac{L_2(r_s, x, t)}{T(r_s, x, t)}; \;\; D_{xt} = \frac{L_T(r_s, x, t)}{T(r_s, x, t)}; D_t = \frac{T_2(r_s, x, t)}{T(r_s, x, t)}; \Lambda = \frac{1 - P(r_s, x, t)}{T(r_s, x, t)}$$

Here, the parameters have the form of (cf. Eq. (58)):

$$L(r_s, x, t) = \int \; lP(r_s, l, r_p)\psi(l, \tau \mid r_s, r_p, x, t) dl d\tau dr_p;$$

$$T(r_s, x, t) = \int \; \tau P(r_s, l, r_p)\psi(l, \tau \mid r_s, r_p, x, t) dl d\tau;$$

$$L_2(r_s, x, t) = \int \; l^2 P(r_s, l, r_p)\psi(l, \tau \mid r_s, r_p, x, t) dl d\tau;$$

$$T_2(r_s, x, t) = \int \; \tau^2 P(r_s, l, r_p)\psi(l, \tau \mid r_s, r_p, x, t) dl d\tau;$$

$$L_T(r_s, x, t) = \int \; l\tau P(r_s, l, r_p)\psi(l, \tau \mid r_s, r_p, x, t) dl d\tau;$$

$$P(r_s, x, t) = \int \; P(r_s, l, r_p)\psi(l, \tau \mid r_s, r_p, x, t) dl d\tau$$

All of these parameters are determined in terms of the flight distribution $\psi(l,\tau \mid r_s, r_p, x, t)$. Hence, according to Eq. (63), they depend on the local flight distribution. The expression for them also involves the passing probability $P(r_s, l, r_p)$, since the average distances, times and second moments of the particle flights are only calculated for the particles that pass the pores. The last equation gives an a posteriori probability of passing a pore at a given point (unlike a priori probability $P(r_s, l, r_p)$ discussed above). Evidently, the a posteriori probability for a particle to be captured at a given point is defined as $p(r_s, x, t) = 1 - P(r_s, x, t)$.

Let us now formulate the equation for the evolution of the pore size distribution $H(l, r_p, x, t)$. For simplicity of discussion, we assume that each captured particle closes one pore (otherwise we had to introduce other a priori characteristics similar to $p\left(r_s, r_p \to r_p^{'}\right)$, similar to Section 2.1.1). Capturing one particle of the size r_s in a certain pore (l, r_p) happens, on average, $p(r_s, l, r_p) / T(r_s, x, t)$ times per second. Therefore, the equation for evolution of the pore size distribution may be represented in the form of

$$\frac{\partial H(l, r_p, x, t)}{\partial t} = -f(l, r_p, x, t) \int \frac{p(r_s, l, r_p)}{T(r_s, x, t)} C(r_s, x, t) dr_s \tag{64}$$

This equation resembles the population balance equation (11), with the main difference that the assumption about complete capturing results in the absence of the positive source term. A more detailed substantiation of Eq. (64) is given in [50].

Equations (61), (64) form a closed system for particle size distribution $C(r_s, x, t)$ and pore size distribution $H(l, r_p, x, t)$, as far as evolutions of velocity and porosity are known (they are used in the definition (62) of the a priori function $\psi(\tau \mid r_s, l, r_p, x, t)$). While velocity for an incompressible flow may be treated as a constant or a known function of time, the porosity may be expressed on the basis of $H(l, r_p, x, t)$. This finally closes the system. The equations forming this system are connected, since the coefficients in Eq. (61) depend on $H(l, r_p, x, t)$. This dependence expresses the fact that the particles in a flowing suspension "compete" for the porous space. In the dilute suspensions, coefficients in Eq. (61) may be treated as constants, and the equations become decoupled.

4.3. Upscaling

System of equations (61), (64) is, at least, as difficult to solve as a system of equations for the population balances (15), (16) considered in Section 2. These equations are integral-differential and non-linear. For a polydisperse suspension consisting of the particles of n different distinct sizes, upscaling is possible, similar to the methods developed in Section 2.2. For the suspension consisting of particles of n distinct sizes, concentration $C(r_s, x, t)$ is

represented by the set of concentrations $\{c_i(x,t), i=1,...,n\}$ corresponding to the different sizes r_{si}, and Eq. (64) is reduced to

$$\frac{\partial H(l,r_p,x,t)}{\partial t} = -\frac{H(l,r_p,x,t)}{h(x,t)}\sum_{i=1}^{n}\frac{p_i(l,r_p)}{T_i(x,t)}c_i(x,t)$$

Again, similar to Section 2.2, we look for the solution of this equation in the form of $H(l,r_p,x,t) = H(l,r_p,x,h_1,...,h_n)$, where unknown functions $h_i(x,t)$ are determined from the equations

$$\frac{\partial h_i(x,t)}{\partial t} = -\frac{c_i(x,t)}{h(x,t)T_i(x,t)} = -\frac{c_i(x,t)}{h(x,h_1,...,h_n)T_i(x,h_1,...,h_n)}\ (i=1,...,n) \qquad (65)$$

with initial conditions

$$h_i(x,0) = 0 \qquad \textbf{(66)}$$

According to the chain rule, this leads to equations for H:

$$\frac{\partial H}{\partial h_i} = p_i(l,r_p)H,$$

which are all obeyed by function H having the form of

$$H(l,r_p,x,h_1,...,h_n) = H_0(l,r_p,x)\exp\left[\sum_{i=1}^{n}p_i(l,r_p)h_i\right] \qquad (67)$$

With such a function H, the coefficients in Eq. (61) become dependent of $h_1,...,h_n$, and it is reduced to

$$\frac{\partial c_i}{\partial t} + v_i(x,\{h_j\})\frac{\partial c_i}{\partial x} =$$
$$D_{x,i}(x,\{h_j\})\frac{\partial^2 c_i}{\partial x^2} + D_{xt.i}(x,\{h_j\})\frac{\partial^2 c_i}{\partial x \partial t} + D_{t,i}\frac{\partial^2 c_i}{\partial t^2} - \Lambda_i(x,\{h_j\})c_i \qquad (68)$$
$$(i=1,...,n)$$

Equations (65), (68) form a closed system of $2n$ equations for $2n$ variables h_i, c_i. This system is similar to the system of equations (35), (36) obtained on the basis of the population balances, apart from the following distinctions. First, system (35), (36) incorporates porosity and expresses the transport in terms of the macroscopic (superficial) flow velocity U. Meanwhile, the system above incorporates hydrodynamic (interstitial) flow velocities v_i. This distinction between the systems may partly be overcome by the multiplication of Eq. (68) by porosity and the corresponding re-designations of the coefficients. The particles of the different sizes, according to Eq. (68), are allowed to move with the different velocities, while system (35) describes a population flowing with the same convective velocity. This difference is due to physical simplifications applied in Section 2. Individual corrections to the particle velocities may be introduced in the framework of the population balance approach [37].

A more important difference is the presence of the dispersive terms in Eq. (68) and, especially of the elliptic dispersive term $D_{t,i}\partial^2 c_i / \partial t^2$. This term expresses the temporal dispersion of the particle flight, in the same manner as the standard diffusive term $D_{x,i}\partial^2 c_i / \partial x^2$ expresses its spatial dispersion. The mechanism of dispersion of the flight times seems to be difficult to introduce in the framework of the population balance approach (although, of course, the corresponding terms may always be formally introduced).

The equations for h_i are also slightly different from those derived in Section 2. This difference is due to a more "individual" approach to particle capturing in the framework of the elliptic formalism compared to the population balance model.

It is seen that the complexity of the averaged system increases with the polydispersity of the suspension. The number of equations is proportional to the number of the distinct particle sizes. Numerical methods are required for solution of the system (65) – (67), as discussed below.

4.4. Solution

A system of integro-differential equations (61), (64), or, similarly, a system of ODE-PDE (65), (68) needs initial and boundary conditions. The main problem here is to specify initial conditions, since the system contains the second time derivatives of the concentrations. This problem was considered in [44, 45, 50].

The second derivative of the concentration by time requires, in principle, two initial conditions. Meanwhile, it is physically evident that a single initial condition should be sufficient for the considered process. On the other hand, specification of the two initial conditions at the same time moment would lead to an instable elliptic problem.

It was proven in [44] for a "standard" elliptic equation $c_t = D_x c_{xx} + D_t c_{tt}$ that, for bounded boundary conditions, the equation has the only solution that does not tend to infinity as $t \to \infty$. This is the only physically reasonable solution obeying the mass conservation law. However, the condition of limitedness at infinity is not convenient for numerical computations. In order to overcome this problem, one may postulate the "final" boundary conditions at some time T, which should be selected from physical considerations.

Consider, for example, a typical experimental problem of injecting a finite portion of the suspension during time $0 < t < T_0$. After that time, pure carrying liquid is injected. Then it

may be assumed that after time T, which is large enough, there will be no (or almost no) suspended concentration in the flow. As shown in [50], for practical calculations, it is sufficient to set $T = 5T_0$.

The boundary conditions for system (65), (68) may be the same as for the classical ADE system. In this respect, statement of the boundary problem for this system is easier that for the complete CTRW approach.

Simultaneous discretization of Eqs. (65), (68) may also be rather cumbersome. It was suggested in [50] (in different terms) to apply an iterative method where, in one cycle, first concentrations c_i are found under known h_i, and then h_i are recalculated with c_i known from the previous iteration. The method was shown to converge after 3-4 iterations, at least for the problems investigated.

4.5. Experimental Verification

Verification of the formalism developed above requires the flooding experiments with observations of the breakthrough curves and deposition profiles. The breakthrough curves predicted on the basis of the elliptic formalism are usually more dispersed compared to the Fickian approach, while the resulting deposition profiles are usually hyper-exponential: the dependence of the deposition amount logarithm on the distance is convex (Figure 1). It has been shown [26-28, 30, 40] that such phenomena are usually observed in the experiments conducted with highly heterogeneous porous media.

In most of the laboratory flooding experiments, the porous media may vary from homogeneous packed glass beads and uniformly packed sands to non-uniformly packed sands and natural porous media (underground formations). The elliptic equation with distributed filtration coefficients can be applied to simulate both tracer transport and colloid flow in porous media of varying heterogeneity [11, 46]. For highly heterogeneous porous media, the elliptic equation approach excels the Fickian approach in matching both the breakthrough curve and deposition profiles. For nearly homogeneous or slightly heterogeneous porous media, the elliptic or CTRW formalism is not necessary for modeling, but the particle distribution may still be needed to model the deposition curves, requiring the application of the population balance approach.

The degree of "wash-out" of a breakthrough curve indicates whether accounting for distribution of the times of flight is necessary. In cases where a breakthrough curve is (almost) stepwise (which is commonly observed for uniform, especially, artificial porous media), application of the elliptic formalism seems to be inadequate, and hyper-exponentiality of the deposition profiles, if observed, should be caused by the explicit or implicit distribution of the parameters of the particles in the suspension. In non-uniform porous media, the breakthrough curves may be more dispersed. For such cases, the elliptic transport equation, probably, coupled with the particle distribution, seems to be more adequate. It should be remarked that the spatial dispersion alone does not lead to sufficient wash-out of the breakthrough curves. At least, in all of the cases studied by us [11, 46], introduction of the term containing second time derivative was necessary in order to match the experimental data.

Uncertainty and sensitivity analysis of the elliptic equation modeling colloids filtration was performed in Ref. [46]. It was shown that the model parameters can be uniquely identified in the case of small-scale median heterogeneity (uniform heterogeneity or randomly packed), while this may not be in the case of large-scale heterogeneity (heterogeneity scale comparable to the column). The parameters for distributed particle properties (filtration coefficients) are correlated and may not be uniquely identified for all cases. This indicates a certain limitation of the elliptic formalism as applied to non-Fickian transport in the porous media of small-scale heterogeneity. For large-scale heterogeneity, finer grids of discretization and multi-dimensional modeling are required.

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