Understanding the Non-Gaussian Nature of Linear Reactive Solute Transport in 1D and 2D

From Particle Dynamics to the Partial Differential Equations

**Gerard Uffink · Amro Elfeki · Michel Dekking ·
Johannes Bruining · Cor Kraaikamp**

Abstract   In the present study, we examine non-Gaussian spreading of solutes subject to advection, dispersion and kinetic sorption (adsorption/desorption). We start considering the behavior of a single particle and apply a random walk to describe advection/dispersion plus a Markov chain to describe kinetic sorption. We show in a rigorous way that this model leads to a set of differential equations. For this combination of stochastic processes, such a derivation is new. Then, to illustrate the mechanism that leads to non-Gaussian spreading, we analyze this set of equations at first leaving out the Gaussian dispersion term (microdispersion). The set of equations now transforms to the telegrapher's equation. Characteristic for this system is a longitudinal spreading that becomes Gaussian only in the longtime limit. We refer to this as kinetics-induced spreading. When the microdispersion process is included back again, the characteristics of the telegraph equations are still present. Now, two spreading phenomena are active, the Gaussian microdispersive spreading plus the kinetics-induced non-Gaussian spreading. In the long run, the latter becomes Gaussian as well. Another non-Gaussian feature shows itself in the 2D situation. Here, the lateral spread and the longitudinal displacement are no longer independent, as should be the case for a 2D Gaussian spreading process. In a displacing plume, this interdependence is displayed as a 'tailing' effect. We also analyze marginal and conditional moments, which confirm this result. With respect to effective properties (velocity and dispersion), we conclude that effective parameters can be defined properly only for large times (asymptotic times). In the two-dimensional case, it appears that the transverse spreading depends on the longitudinal coordinate. This results in 'cigar-shaped' contours.

G. Uffink (✉) · J. Bruining
Department of Civil Engineering and Geosciences, Delft University of Technology, Stevinweg 1,
2628 CN, Delft, The Netherlands
e-mail: G.J.M.Uffink@tudelft.nl

A. Elfeki
Department of Water Resources, Faculty of Metereology, Environment and Arid Land Agriculture,
King Abdul Aziz University, Jeddah, Saudi Arabia

M. Dekking · C. Kraaikamp
Department EWI (DIAM), Delft University of Technology, Mekelweg 4, 2628 CD, Delft, The Netherlands

1 Introduction

It is well known that in the field a contaminant plume spreads at a higher rate than as predicted by theory and laboratory experiments. In addition, one observes that the spreading pattern often deviates from the Gaussian pattern, especially at early times (tailing). These phenomena have been analyzed intensively, theoretically, numerically and by field experiments (Gelhar et al. 1979; Neuman et al. 1987; Dagan 1988; Dieulin et al. 1981a,b; Scheidegger 1959; Biggar and Nielsen 1962; Maloszewski and Zuber 1992; Berkowitz et al. 2006; Dentz and Castro 2009; Dentz and Tartakovsky 2006; Schumer et al. 2003). Many papers on this subject attribute non-Gaussian behavior to the heterogeneity of the medium. In a homogeneous aquifer, a similar behavior occurs when contaminants are subject to a relatively slow kinetic adsorption/desorption reaction.

We consider a homogeneous medium and follow a (solute) particle during its motion through the pore system, while simultaneously it is subject to adsorption/desorption. Although the porous medium itself is simply homogeneous and non-stochastic, the particle's behavior is still chaotic and, therefore, our particle model will be stochastic. Note that our approach differs from that of papers on particle tracking in the sense that we do not start with the advection–dispersion–reaction equations and, accordingly, perform a particle tracking algorithm to solve or simulate the equations. Instead, we start with a stochastic description for the movement of a single particle and work our way towards the differential equations. Frequently, particle tracking papers on advection-dispersion with kinetic sorption assume an analogy between particle tracking and the differential equations by just stating the validity of this analogy (e.g. Valocchi and Quinodoz 1989; Valocchi 1988). To our knowledge, a rigorous derivation of the differential equations for advective-dispersive transport with kinetic sorption starting from a stochastic model for a single particle does not exist in any of those papers (in the absence of dispersion a similar derivation is given in Mishra et al. 1999, p.554). The paper by Benson and Meerschaert (2009) provides an alternative rigorous derivation based on a time change approach (also known as subordination).

We also discuss particle models used in various other fields, such as the velocity jump model (chemotaxis or movement of bacteria, Hillel 1995). This velocity jump model (or Giddings–Eyring model, e.g. Giddings and Eyring 1955) leads to a telegraph equation. It differs from our model by the fact that there is no diffusion or dispersion phenomenon. We will demonstrate that, when the velocity jump is extended with dispersion/diffusion, the telegraph character stills remains. This explains the non-Gaussian behavior in the pre-asymptotic stage.

The non-Gaussian features can also be illustrated by (spatial) moments, especially by the third (skewness) and fourth (kurtosis) centralized moments. For the 1D situation, first and second moments were studied by previous authors e.g. Valocchi (1988), Chrysikopoulos et al. (1992) and Souadnia et al. (2002). These papers mainly focused on the large time (asymptotic) results. Pre-asymptotic expressions for first and second moments were first derived by Michalak and Kitanidis (2000). Unfortunately, in the formulation of the solutions, Michalak and Kitanidis suggest that for an arbitrary initial distribution of the phases the mean and variance in each separate phase can be obtained by a linear combination. However, this is only true for the non-centralized moments, but not for the variance. Moreover, one of the 4 solutions is incorrect (see Sect. 5.1, and also Dekking and Kong 2011a,b).

In our paper, we shall consider the moments for the 2D situation and examine in detail the conditional moments. These moments manifest more clearly the non-Gaussian behavior than the 1D or marginal moments. It shows that non-Gaussian behavior can exist, even when the marginal moments suggest that the behavior is Gaussian.

In our 'particle view', the behavior of a particle is described by a random walk and a two-state Markov process. A similar model was used by Valocchi (1988), Valocchi and Quinodoz (1989) and Van Kooten (1996). Equivalent processes occur in other fields, such as chromatography (Giddings and Eyring 1955; Giddings 1963; Keller and Giddings 1960) or in statistical physics (e.g. Fürth 1920; Goldstein 1951; Kac 1956; Weiss 2002 and Masoliver and Weiss 1996).

In groundwater solute transport, a concept with some similarity to kinetic sorption is that of the dual porosity. The dual porosity concept was introduced in a pioneering paper by Barenblatt et al. (1960). It defines solute concentrations both in a flowing and in a stagnant fluid phase. In the general description, the full time dependence of the diffusion into the stagnant phase has to be taken into account, in which case we obtain an integro-differential equation (De Smedt and Wierenga 1979). This equation can also be handled with the use of temporal moments (Harvey and Gorelick 1995). The mass transfer between stagnant and flowing phase is often simplified by a forward and backward rate expression analogous to model of kinetics sorption. This simplified approach has been validated by numerous experiments (Coats and Smith 1964; Haggerty et al. 2004; Nkedi-Kizza et al. 1984; Roth and Jury 1993; Van Genuchten and Wierenga, 1977). The kinetic sorption model and dual porosity model can be shown to be equivalent for many conditions of practical interest (Haggerty and Gorelick 1995; Nkedi-Kizza et al. 1984), in particular in the longtime limit (Van Genuchten and Wierenga 1976; Carrera et al. 1998; Haggerty et al. 2000).

Several authors (e.g. Attinger et al. 1999; Dentz and Castro 2009) study sorptive-advective-dispersive solute transport using the concept of a retardation coefficient, assuming that sorption has reached an equilibrium. Such a model is less complex than kinetic (non-equilibrium) sorption, but the authors give interesting applications for retardation factors that vary randomly according to some stochastic models. These studies, e.g. Dentz and Bolster (2010) and Dentz and Tartakovsky (2006) focus on the non-Gaussian features of the transport as a consequence of a heterogeneous velocity field. In a homogeneous medium with constant sorption parameters, non-Gaussianity may also arise as the result of the sorption kinetics, as shown, e.g., by 1D examples given by Roth and Jury (1993). In our paper, we make this more explicit and also discuss the 2D situation.

The particle approach used in our paper is the classical or discrete time random walk, where particles perform steps of a random size but in a (fixed) period of time, Δt. The differential equation describing advection, dispersion and kinetic sorption is obtained letting $\Delta t \to 0$ in the diffusion limit. An alternative method frequently encountered in the recent literature is the continuous time random walk (CTRW) originally introduced by Montroll and Weiss (1965), Weiss (1994). An early application of this model to the trapping of electrons is given in Schmidlin (1977). In the CTRW, the particle moves in space in a number of jumps, n, each step occurring in a time interval that varies randomly according to a step probability function. This function is also called the memory function by some authors. The amount of steps remains a finite, discrete (and random) number, unlike in the approach used in our paper, where the number of steps approaches infinity and $\Delta t \to 0$. The CTRW leads to a different formulation, where the differential equations are finally obtained via Laplace transforms. There exists an extensive literature on applications of CTRW describing plume properties in relation to aquifer heterogeneity, see e.g. Dentz and Berkowitz (2003), Schumer et al. (2003), Dentz et al. (2004) and Salamon et al. (2006). Sorption can be included, which is

done often by introducing a retardation factor, based on the assumption of local equilibrium, see e.g. Dentz and Castro (2009). Margolin et al. (2003), however, show that kinetic sorption can also be taken into account by modifying the step probability function. Non-Gaussianity may also be built in via the step probability function. Extensive reviews of the method can be found in Bouchaud and Georges (1990) and Berkowitz et al. (2006). For a more general review on the different random walk approaches including CTRW, see Delay et al. (2005).

2 The Particle View

2.1 A Stochastic Particle Model

We model the movement of a single particle subject to an advection/dispersion/sorption process over a time interval $[0, t]$. For simplicity, we discuss the one-dimensional case. We discretize time by choosing some n and by dividing $[0, t]$ into n intervals of length $\Delta t = t/n$. We observe the state of the particle at the time points $0, \Delta t, 2\Delta t, \ldots, n\Delta t$. For this state, there are two possibilities: 'free' or 'adsorbed,' which we code by the letters f and a. The particle can only move when it is 'free,' and its displacement has two components: dispersion and advection.

Let X_k be the displacement due to the dispersion of the particle the kth time that it is 'free.' We model the X_k as independent random variables with mean and variance

$$\mathrm{E}\,[X_k] = 0 \quad \text{and} \quad \mathrm{Var}\,(X_k) = 2D\Delta t.$$

The displacement due to advection is given by $v\Delta t$, where v is the (deterministic) advection velocity.

Let K_n be the number of intervals $[k\Delta t, (k+1)\Delta t)$ during $[0, t]$ that the particle was 'free.' (Here, the open bracket at the right end indicates that the point $(k+1)\Delta t$ is not included.) In other words, $K_n \Delta t$ is the free residence time of the particle in $[0, t]$. Let $S(t)$ be the position of the particle at time t. Combining the two types of displacement, we obtain

$$S(t) = \sum_{k=1}^{K_n} (X_k + v\Delta t).$$

The distribution of K_n is determined by the kinetics, i.e., by the switching between the 'free' and the 'adsorbed' state. This is naturally described by a two-state Markov chain. The state transitions of this chain after a certain time step Δt are given by a transition probability matrix (p_{ij}):

$$\begin{bmatrix} p_{ff} & p_{fa} \\ p_{af} & p_{aa} \end{bmatrix} = \begin{bmatrix} 1-b & b \\ a & 1-a \end{bmatrix}. \tag{1}$$

This means that for instance the transition from 'adsorbed' to 'free' has probability $a = p_{af}$ to happen during the time interval $[k\Delta t, (k+1)\Delta t)$ (note that actually we make this change—if it takes place—at the end of the interval).

We will be mainly interested in the moments of $S(t)$. Below, we will compute the first and second moments, and in the next section, we discuss the (centered) third and fourth moments. To compute $\mathrm{E}\,[S(t)]$, we use the well-known formula (see e.g. Ross 2000) for a random sum

of K_n independent and identically distributed random variables Y_k (also independent of K_n):

$$\mathrm{E}\left[\sum_{k=1}^{K_n} Y_k\right] = \mathrm{E}[K_n]\,\mathrm{E}[Y_1].$$

Here, the mean of K_n equals:

$$\mathrm{E}[K_n] = \frac{a}{a+b}\,n.$$

This expression can be obtained from Viveros et al. (1994), or Dekking and Kong (2011a,b). Substituting this, we find (with $n\Delta t = t$)

$$\mathrm{E}[S(t)] = \mathrm{E}[K_n]\,(\mathrm{E}[X_1 + v\Delta t]) = \frac{a}{a+b}\,vt. \tag{2}$$

Here, $(a+b)/a$ is the retardation factor R. To see this, note that the probability vector $\big(b/(a+b) \quad a/(a+b)\big)$ is the stationary distribution of the Markov chain, and so $a/(a+b)$ is the fraction of time the particle is free. Thus, the effective velocity $v^* = v/R$. We have implicitly required that the particle at time 0 is given the state 'adsorbed' or 'free' according to this distribution, and for other initial distributions, there will be a correction term in the formula for $\mathrm{E}[S(t)]$, which tends to 0 as t tends to infinity (cf. Dekking and Kong 2011a,b).

To compute $\mathrm{Var}(S(t))$, we use the well-known formula (see e.g. Ross 2000) for the *variance* of a random sum of K_n i.i.d. random variables Y_k (also independent of K_n):

$$\mathrm{Var}\left(\sum_{k=1}^{K_n} Y_k\right) = \mathrm{E}[K_n]\,\mathrm{Var}(Y_1) + \mathrm{Var}(K_n)\,(\mathrm{E}[Y_1])^2. \tag{3}$$

This yields with $Y_k = X_k + v\Delta t$ and $n\Delta t = t$:

$$\begin{aligned}
\mathrm{Var}(S(t)) &= \mathrm{E}[K_n]\,\mathrm{Var}(X_k + v\Delta t) + \mathrm{Var}(K_n)\,(\mathrm{E}[X_k + v\Delta t])^2 \\
&= \frac{a}{a+b}\,2D\,t + \mathrm{Var}(K_n)\,v^2(\Delta t)^2,
\end{aligned} \tag{4}$$

where [as can be deduced from Viveros et al. (1994) or Dekking and Kong (2011a,b)]

$$\mathrm{Var}(K_n) = \frac{ab(2-a-b)}{(a+b)^3}\,n - \frac{2ab(1-a-b)}{(a+b)^4}[1-(1-a-b)^n]. \tag{5}$$

The Eqs. (4) and (5) thus tell us that the variance of the displacement of the particle grows more or less linearly in time with (asymptotic) slope

$$\frac{a}{a+b}2D + \frac{ab(2-a-b)}{(a+b)^3}v^2\Delta t.$$

2.2 Skewness and Kurtosis

To obtain the skewness of $S(t)$, we must use the not so well-known formula for the *third central moment* of a random sum of K_n i.i.d. random variables Y_k (also independent of K_n):

$$\begin{aligned}
\mathrm{E}\left[(S(t) - \mathrm{E}[S(t)])^3\right] &= \mathrm{E}\left[\left(\sum_{k=1}^{K_n} Y_k - \mathrm{E}\left[\sum_{k=1}^{K_n} Y_k\right]\right)^3\right] \\
&= \mathrm{E}[K_n]\,\mathrm{E}\left[(Y_1 - \mathrm{E}[Y_1])^3\right] + 3\mathrm{E}[Y_1]\,\mathrm{Var}(Y_1)\,\mathrm{Var}(K_n) \\
&\quad + (\mathrm{E}[Y_1])^3\,\mathrm{E}\left[(K_n - \mathrm{E}[K_n])^3\right].
\end{aligned}$$

To actually derive a formula for the skewness of the displacement of the particle from this equation will lead to very heavy computations (and the situation for the kurtosis is even worse). However, without doing any computations, we can already tell that as $t \to \infty$, the skewness must tend to zero and the kurtosis to 3: this is because the distribution of the displacement of the particle will tend to a Gaussian by the central limit theorem for *random* sums of independent identically distributed random variables. In our case, this follows since K_n/n tends in the mean and hence in probability to $a/(a+b)$, see Feller (1971), p. 258.

2.3 Decreasing the Time Steps

The discrete time steps are somewhat unnatural. We would like to let Δt tend to 0. But then we have to realize that a and b are functions of Δt. Since the probability that the particle changes its state is proportional to the time Δt it is observed (if Δt is not too large), we should put

$$a = \mu \Delta t, \quad b = \lambda \Delta t, \tag{6}$$

where μ and λ are now the *rates* at which the particle switches from 'adsorbed' to 'free' and from 'free' to 'adsorbed'. Substituting this in Eqs (4) and (5), we obtain

$$\mathrm{Var}\,(S(t)) = \frac{\mu}{\lambda + \mu} 2Dt + \frac{\lambda\mu(2 - (\lambda + \mu)\Delta t)}{(\lambda + \mu)^3} v^2 t$$
$$- \frac{2\lambda\mu(1 - (\lambda + \mu)\Delta t)}{(\lambda + \mu)^4} \left[1 - \left(1 - (\lambda + \mu)\frac{t}{n} \right)^n \right] v^2.$$

Letting $\Delta t \to 0$ and hence $n \to \infty$ we obtain

$$\mathrm{Var}\,(S(t)) = \frac{\mu}{\lambda + \mu} 2Dt + \frac{2\lambda\mu}{(\lambda + \mu)^3} v^2 t - \frac{2\lambda\mu}{(\lambda + \mu)^4} \left[1 - \mathrm{e}^{-(\lambda+\mu)t} \right] v^2. \tag{7}$$

Thus, we recuperate a (more general and more detailed) version of the main result of Gut and Ahlberg (1981), *and* there is a match with the expression that comes from the moment analysis based on the differential equations (as can be derived by correcting the results in Michalak and Kitanidis (2000)).

2.4 The State of the Particle at Time t

Let $S_f(t)$ be the position of the particle at time t *given* that it is free at time t.

To find the distribution of $S_f(t)$, we need the distribution of $K_n^{(f)}$, the number of intervals $[k\Delta t, (k+1)\Delta t)$ during $[0, t]$ that the particle was free, given that it is free at time $t = n\Delta t$. We find now (where $\mathrm{E}\left[K_n^{(f)} \right]$ can be deduced from Viveros et al. 1994) that:

$$\mathrm{E}\left[S_f(t) \right] = \mathrm{E}\left[K_n^{(f)} \right] v \Delta t$$
$$= \left[\frac{a}{a+b} n + \frac{b\left(1 - (1 - a - b)^n \right)}{(a+b)^2} \right] v \Delta t$$
$$= \frac{a}{a+b} vt + \frac{b\left(1 - (1 - a - b)^{t/\Delta t} \right)}{(a+b)^2} v \Delta t.$$

Substituting $a = \mu \Delta t$, $b = \lambda \Delta t$, and letting $\Delta t \to 0$ we obtain

$$\mathrm{E}\left[S_f(t) \right] = \frac{\mu}{\lambda + \mu} vt + \frac{\lambda v}{(\lambda + \mu)^2} \left(1 - \mathrm{e}^{-(\lambda+\mu)t} \right). \tag{8}$$

From Dekking and Kong (2011a,b), we have that $\text{Var}\left(K_n^{(f)}\right)$ equals

$$\left[\frac{a\,b\,(2-a-b)}{(a+b)^3} + \frac{2\,b\,(a-b)\,(1-a-b)^n}{(a+b)^3}\right] n$$

$$+ \left[\frac{b\,(3\,a-b)}{(a+b)^3} - \frac{4\,a\,b}{(a+b)^4}\right]\left[1-(1-a-b)^n\right] + \frac{b^2}{(a+b)^4}\left[1-(1-a-b)^{2n}\right].$$

Using Eq. (3) we derive from this

$$\text{Var}\left(S_f(t)\right) = \text{E}\left[K_n^{(f)}\right]\text{Var}\left(X_k + v\Delta t\right) + \text{Var}\left(K_n^{(f)}\right)(\text{E}\left[X_k + v\Delta t\right])^2$$

$$= \frac{a}{a+b}\,2Dt + \text{Var}\left(K_n^{(f)}\right)v^2(\Delta t)^2 + \frac{b\,(1-(1-a-b))^{t/\Delta t}}{(a+b)^2}2D\Delta t.$$

Substituting $a = \mu\Delta t$, $b = \lambda\Delta t$, and letting $\Delta t \to 0$ we obtain

$$\text{Var}\left(S_f(t)\right) = \frac{\mu}{\lambda+\mu}\,2Dt + \frac{\lambda}{(\lambda+\mu)^2}\left(1-e^{-(\lambda+\mu)t}\right)2D$$

$$+ \left[\frac{2\lambda\mu}{(\lambda+\mu)^3} + \frac{2\lambda(\mu-\lambda)}{(\lambda+\mu)^3}e^{-(\lambda+\mu)t}\right]v^2t$$

$$- \frac{4\lambda\mu}{(\lambda+\mu)^4}\left[1-e^{-(\lambda+\mu)t}\right]v^2 + \frac{\lambda^2}{(\lambda+\mu)^4}\left[1-e^{-2(\lambda+\mu)t}\right]v^2. \quad (9)$$

It can be shown that this matches with the expressions in Michalak and Kitanidis (2000), when these are corrected as in Dekking and Kong (2011a,b). Similar computations can be made for the displacement of the particle *given* that it is absorbed at time t.

2.5 Derivation of the Differential Equations

We will now show how the fundamental differential Eqs. (15), (16) can be obtained from a diffusion limit of the single particle model. Our approach is similar to the one followed for transport in fluidized beds in Dehling et al. (2000).

In order to obtain this diffusion limit, we extend the model of the previous section by also discretizing space in locations

$$i\Delta x, \quad i = \ldots, -1, 0, 1, \ldots.$$

Here, we let Δx depend on Δt in the classical way, which is motivated by the fact that typically at time t the spatial fluctuations are of order $\sqrt{t}$:

$$\Delta x = c\sqrt{\Delta t}, \quad (10)$$

where $c > 0$ will be chosen later. Relation (10) forms the basis for all diffusion processes and goes back to Einstein.

The particle moves according to a Markov chain (Z_n), which is a birth–death process (birth=one step to the right, death=one step to the left), with the additional possibility that the particle may become adsorbed and free again. The state space is therefore a product

$$S = \{\ldots, -1, 0, 1, \ldots\} \times \{a, f\},$$

where, e.g., $Z_n = (i, a)$ means that at time $n\Delta t$ the particle is at $i\Delta x$ and is absorbed.

Let β_i, δ_i and α_i be the probabilities that the particle (in the free state) moves from $i\Delta x$ to $(i+1)\Delta x$ and from $i\Delta x$ to $(i-1)\Delta x$ or stays at $i\Delta x$. Note that in this model the dispersion

Fig. 1 The three possible movements of the particle when it is free

$$\alpha_i$$
$$\delta_i \qquad \beta_i$$
$$(i-1)\Delta x \qquad i\Delta x \qquad (i+1)\Delta x$$
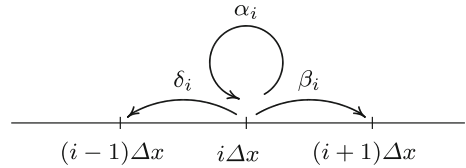
may depend on the location, i.e., we could more generally consider (deterministic) inhomogeneous media. To make this more realistic, we could also let the adsorption and desorption rates depend on i. As we consider here only the homogeneous case, we take $\beta_i = \beta$, $\delta_i = \delta$ and $\alpha_i = \alpha$ for each i. To fit the new model with the model in Sect. 2.1, we choose values for β, δ and α in the following fashion: (Fig.1)

$$\beta = D\frac{\Delta t}{(\Delta x)^2} + \frac{v^2}{2}\Big(\frac{\Delta t}{\Delta x}\Big)^2 + \frac{v}{2}\frac{\Delta t}{\Delta x}$$

$$\delta = D\frac{\Delta t}{(\Delta x)^2} + \frac{v^2}{2}\Big(\frac{\Delta t}{\Delta x}\Big)^2 - \frac{v}{2}\frac{\Delta t}{\Delta x}$$

$$\alpha = 1 - \beta - \delta = 1 - 2D\frac{\Delta t}{(\Delta x)^2} - v^2\Big(\frac{\Delta t}{\Delta x}\Big)^2.$$

By fitting, we mean that the mean and the variance of the displacement in a time interval of length Δt of the particle (in the free state) are the same in the two models. Indeed, the mean of this displacement equals $\beta\Delta x - \delta\Delta x = v\Delta t$, and the variance equals

$$\beta(\Delta x)^2 + \delta(\Delta x)^2 - (v\Delta t)^2 = 2D\Delta t.$$

In terms of Δt only, using (10), the displacement probabilities are

$$\beta = \frac{D}{c^2} + \frac{v^2\Delta t}{2c^2} + \frac{v\sqrt{\Delta t}}{2c}$$

$$\delta = \frac{D}{c^2} + \frac{v^2\Delta t}{2c^2} - \frac{v\sqrt{\Delta t}}{2c}$$

$$\alpha = 1 - \frac{2D}{c^2} - \frac{v^2\Delta t}{c^2}.$$

From this, we see that these are indeed probabilities for Δt small enough, provided we choose $c > \sqrt{2D}$. The possible transitions of the chain are

The corresponding transition probabilities are:

$$p_{(i,f),(i+1,f)} = \beta(1 - \lambda\Delta t) \quad p_{(i,f),(i+1,a)} = \beta\lambda\Delta t$$

$$p_{(i,f),(i-1,f)} = \delta(1 - \lambda\Delta t) \quad p_{(i,f),(i-1,a)} = \delta\lambda\Delta t$$

$$p_{(i,a),(i,a)} = 1 - \mu\Delta t \quad p_{(i,a),(i,f)} = \mu\Delta t$$

$$p_{(i,f),(i,f)} = \alpha(1 - \lambda\Delta t) \quad p_{(i,f),(i,a)} = \alpha\lambda\Delta t$$

Let $p_f(i, n)$, respectively $p_a(i, n)$, be the probability that at time $t = n\Delta t$ the particle is free, respectively, absorbed and at position $i\Delta x$.

The master equations or Chapman–Kolmogorov equations for the particle are

$$p_f(i, n+1) = p_f(i-1, n)\beta(1 - \lambda\Delta t) + p_f(i+1, n)\delta(1 - \lambda\Delta t)$$
$$+ p_f(i, n)\alpha(1 - \lambda\Delta t) + p_a(i, n)\mu\Delta t, \tag{11}$$

and

$$p_a(i, n+1) = p_f(i-1, n)\beta\lambda\Delta t + p_f(i+1, n)\delta\lambda\Delta t$$
$$+ p_f(i, n)\alpha\lambda\Delta t + p_a(i, n)(1 - \mu\Delta t). \tag{12}$$

With some abuse in notation regarding the functions p_a and p_f, we will denote the limiting probabilities of $p_a(i, n)$ and $p_f(i, n)$ as $i\Delta x \to x$, and $t = n\Delta t$ by $p_a(x, t)$ and $p_f(x, t)$. We will obtain partial differential equations for these limiting probabilities when we let $\Delta t \to 0$, and $i = i(\Delta t) \to \infty$, in such a way that $i\Delta x \to x$. (The obvious way to achieve this is to take $i(\Delta t)$ equal to the integer closest to $x/(c\sqrt{\Delta t})$.) Rearranging (11) we obtain

$$p_f(i, n+1) = p_f(i-1, n)\beta + p_f(i+1, n)\delta + p_f(i, n)\alpha - \lambda\Delta t[p_f(i-1, n)\beta$$
$$+ p_f(i+1, n)\delta + p_f(i, n)\alpha] + p_a(i, n)\mu\Delta t. \tag{13}$$

In the first three terms of the right-hand side, we substitute the values for β, δ and α:

$$p_f(i-1, n)\beta + p_f(i+1, n)\delta + p_f(i, n)\alpha$$
$$= \left[D\frac{\Delta t}{(\Delta x)^2} + \frac{v^2}{2}\left(\frac{\Delta t}{\Delta x}\right)^2\right]\left[p_f(i-1, n) - 2p_f(i, n) + p_f(i+1, n)\right]$$
$$+ \left[\frac{v}{2}\frac{\Delta t}{\Delta x}\right]\left[p_f(i-1, n) + p_f(i+1, n)\right] + p_f(i, n). \tag{14}$$

Substituting Eq. (14) into (13) and dividing by Δt, we obtain an equation for the difference quotient $(p_f(i+1, n) - p_f(i, n))/\Delta t$. Then, letting $\Delta t \to 0$, we obtain

$$\frac{\partial p_f(x, t)}{\partial t} = D\frac{\partial^2 p_f(x, t)}{\partial x^2} - v\frac{\partial p_f(x, t)}{\partial x} - \lambda p_f(x, t) + \mu p_a(x, t). \tag{15}$$

For the adsorbed phase, a similar equation can be derived. Here, since the adsorbed particle is not subject to advection or dispersion, the first and second terms at the right-hand side are absent.

$$\frac{\partial p_a(x, t)}{\partial t} = -\mu p_a(x, t) + \lambda p_f(x, t). \tag{16}$$

2.6 From Particle to Plume

It might seem surprising that we study the behavior of a contaminant plume from the stochastic analysis of a single particle. Here, we illustrate how these two approaches are connected. We model the contaminant plume by a collection of N particles. These particles move independently according to the same law as the single particle considered in the previous sections. Let $S_i(t)$ be the position of the ith particle at time t. We are interested in the centroid $Z(t)$ of the plume at time t. This is given by

$$Z(t) = \frac{1}{N}\sum_{i=1}^{N} S_i(t).$$

We are also interested in the spreading of the plume around its centroid. We measure this by the (empirical) variance $V(t)$ of the particles given by

$$V(t) = \frac{1}{N}\sum_{i=1}^{N}(S_i(t) - Z(t))^2. \tag{17}$$

The random variable $Z(t)$ is an average of independent identically distributed random variables with finite expectation. Therefore by the strong law of large numbers for t fixed, and N large

$$Z(t) \approx \mathrm{E}\,[S(t)]\,. \tag{18}$$

We now turn to the spread of the plume. Here, the situation is more complicated because the terms in the sum are no longer independent random variables and also depend on N. It is well known that a rewriting of Eq. (17) yields

$$V(t) = \frac{1}{N} \sum_{i=1}^{N} (S_i(t) - Z(t))^2$$

$$= \frac{1}{N} \sum_{i=1}^{N} (S_i(t) - \mathrm{E}\,[S(t)])^2 - (Z(t) - \mathrm{E}\,[S(t)])^2\,.$$

We have already argued (see (18)) that the last term is approximately 0, and another application of the law of large numbers to the first term yields that

$$V(t) \approx \mathrm{E}\left[(S(t) - \mathrm{E}\,[S(t)])^2\right] = \mathrm{Var}\,(S(t))\,.$$

3 Giddings–Eyring Model

Now that we have derived the basic Eqs. (15) and (16) we turn to their analysis. To illustrate the spreading induced by the kinetic sorption, we first consider a simpler, but related system, given by the following equations:

$$\frac{\partial N_f(x)}{\partial t} + v \frac{\partial N_f(x)}{\partial x} = \mu N_a(x) - \lambda N_f(x)$$

$$\frac{\partial N_a(x)}{\partial t} = \lambda N_f(x) - \mu N_a(x).$$

The difference with Eqs. (15) and (16) is that the hydrodynamic dispersion process is absent. Also, we have replace the probability densities of a single particles by the (one-dimensional) densities of the large number of particles, denoted by N_f and N_a. This system occurs in the literature under various names. In probability theory and statistical physics, it is known as a persistent or correlated random walk and has been studied e.g. by Fürth (1920), Goldstein (1951), Taylor (1920), Kac (1956), and Weiss (2002). In the field of chromatography, the system is intensively studied as well (Giddings and Eyring 1955; Giddings 1963; Keller and Giddings 1960). Solutions for the probability density functions of the particles are given by Giddings and Eyring, which is why we refer here to this system as the Giddings–Eyring model. Hillel (1995) applies the equations to the movement of bacteria in the direction of the gradient of food molecules (chemotaxis) and uses the term "velocity jump process".

We introduce and analyze the Giddings–Eyring model first, since several interesting observations can be made with respect to the spreading of the particles. The particles are undergoing an 'apparent' dispersion, despite the fact that (hydrodynamic) dispersion is not included in the model. We show that this 'kinetics-induced' dispersion develops in a non-Gaussian way. In the system described by (15) and (16), both hydrodynamic dispersion and the kinetics-induced dispersion are present. When the latter is dominant, non-Gaussian spreading is observed also in systems that includes hydrodynamic dispersion, as we shall illustrate later.

For our analysis, first we introduce a moving coordinate system with velocity v^*. The new x coordinate is:

$$\bar{x} = x - v^*t.$$

where $v^* = v\mu/(\lambda + \mu)$. In the new coordinate system, free particles move to the right with velocity $v_f = v - v^* = v\lambda/(\lambda + \mu)$. The adsorbed particles 'move' with velocity $v_a = -v^* = -v \times \mu/(\lambda + \mu)$. The minus sign indicates that the movement is to the left (i.e. with respect to the new coordinate system). The equations are now:

$$\frac{\partial N_f(\bar{x})}{\partial t} + v_f \frac{\partial N_f(\bar{x})}{\partial \bar{x}} = \mu N_a(\bar{x}) - \lambda N_f(\bar{x})$$

$$\frac{\partial N_a(\bar{x})}{\partial t} + v_a \frac{\partial N_a(\bar{x})}{\partial \bar{x}} = \lambda N_f(\bar{x}) - \mu N_a(\bar{x}).$$

The equations can be rewritten as a single differential equation by considering first the sum and difference of the particle distributions (Kac's trick), i.e.,

$$u(x) = N_f(x) + N_a(x); \quad w(x) = N_f(x) - N_a(x).$$

After summation and substraction of the differential equations, we obtain for u and w:

$$\frac{\partial u}{\partial t} + \left(\frac{\lambda - \mu}{\lambda + \mu}\right) \frac{v}{2} \frac{\partial u}{\partial \bar{x}} + \frac{v}{2} \frac{\partial w}{\partial \bar{x}} = 0$$

$$\frac{\partial w}{\partial t} + \left(\frac{\lambda - \mu}{\lambda + \mu}\right) \frac{v}{2} \frac{\partial w}{\partial \bar{x}} + \frac{v}{2} \frac{\partial u}{\partial \bar{x}} = -u(\lambda - \mu) - w(\lambda + \mu).$$

Now we differentiate the first equation to t and the second to $\bar{x}$ and eliminate the derivatives of w:

$$\frac{\lambda\mu v^2}{(\lambda + \mu)^3} \frac{\partial^2 u}{\partial \bar{x}^2} - \frac{1}{\lambda + \mu} \frac{\partial^2 u}{\partial t^2} - \frac{v(\lambda - \mu)}{(\lambda + \mu)^2} \frac{\partial^2 u}{\partial t \partial \bar{x}} = \frac{\partial u}{\partial t} \qquad (19)$$

This is a telegrapher's equation with an additional term due to asymmetry ($\mu \neq \lambda$). Hillel discusses the symmetrical ($\lambda = \mu$) case only, but Weiss (2002) also makes some remarks on asymmetry. Also see Masoliver and Weiss (1996) and Chandramouli (2002). The telegraph equation may be interpreted either as an advection-dispersion equation with a perturbation term that disappears at large times or as a wave equation with a perturbation term that disappears at early times.

3.1 Large Time Behavior and the Advection-Dispersion Equation

Hillel uses the following argument that leads to a useful result for large times. For large times, the velocity $[LT^{-1}]$ and sorption rates $[T^{-1}]$ typically are expressed in large time units, and thus, their values become large. For example, when time is rescaled by the substitution $t = \omega\tau$ and we introduce velocity v' and sorption rates λ', μ' in the new time units using $v' = \omega v$, $\lambda' = \omega\lambda$ and $\mu' = \omega\mu$, Eq. (19) becomes:

$$\frac{\lambda'\mu'v'^2}{(\lambda' + \mu')^3} \frac{\partial^2 u}{\partial \bar{x}^2} - \frac{1}{\lambda' + \mu'} \frac{\partial^2 u}{\partial \tau^2} - \frac{v'(\lambda' - \mu')}{(\lambda' + \mu')^2} \frac{\partial^2 u}{\partial \tau \partial \bar{x}} = \frac{\partial u}{\partial \tau} \qquad (20)$$

For large times and thus large values of ω, v', λ' and μ' become large. Accordingly, the first term at the left-hand side of (20) dominates over the second and third terms. Therefore,

at large times, the equation approximately describes a dispersion process with an equivalent dispersion coefficient D^*, purely induced by the kinetics:

$$D^* = \frac{\lambda \mu v^2}{(\lambda + \mu)^3} \tag{21}$$

3.2 Short Time Behavior and the Wave Equation

In a similar way, it can be shown that for small times the terms at the left hand remain, while the right side becomes small. The remaining expression is a wave equation that can be written as:

$$\left[\frac{\partial}{\partial t} + \frac{\lambda v}{\lambda + \mu} \frac{\partial}{\partial \bar{x}} \right] \left[\frac{\partial}{\partial t} - \frac{\mu v}{\lambda + \mu} \frac{\partial}{\partial \bar{x}} \right] u = 0$$

or

$$\frac{\partial u}{\partial t} + v_f \frac{\partial u}{\partial \bar{x}} = 0, \quad \frac{\partial u}{\partial t} + v_a \frac{\partial u}{\partial \bar{x}} = 0$$

For an initial pulse at $\bar{x} = 0$, the solution represents two pulses propagating along the characteristics. In $\bar{x}$-space, $\bar{x} - v_f t = 0$ and $\bar{x} - v_a t = 0$, which in x-space correspond to: $x - vt = 0$ and $x = 0$. These pulses can be identified as traveling pulse (original free particles) and a stagnant pulse (the original adsorbed particles).

3.3 Intermediate Time Behavior

The wave equation and diffusion equation are approximations for the process at short and large times, respectively. The intermediate time is described exactly by the full telegraphers's equation. Therefore, examination of the solutions to this equation will give information on the pre-asymptotic spreading behavior of this process.

Solutions for the distribution of the particles have been derived by Giddings and Eyring (see Giddings and Eyring 1955; Giddings 1963 and Keller and Giddings 1960). For detailed discussions of these functions see Van Genuchten and Wierenga (1976), Lassey (1988) and Van Kooten (1996).

Giddings and Eyring consider four types of densities $h_{ff}, h_{af}, h_{fa}, h_{aa}$:

$$\begin{aligned}
h_{ff}(\tau, t) &= e^{-\lambda \tau - \mu(t - \tau)} \sqrt{\frac{\lambda \mu \tau}{t - \tau}} I_1(\theta) + e^{-\lambda t} \delta(t - \tau) \\
h_{fa}(\tau, t) &= \lambda e^{-\lambda \tau - \mu(t - \tau)} I_0(\theta) \\
h_{af}(\tau, t) &= \mu e^{-\lambda \tau - \mu(t - \tau)} I_0(\theta) \\
h_{aa}(\tau, t) &= e^{-\lambda \tau - \mu(t - \tau)} \sqrt{\frac{\lambda \mu(t - \tau)}{\tau}} I_1(\theta) + e^{-\mu t} \delta(\tau),
\end{aligned} \tag{22}$$

where $\tau = x/v$, $\theta = 2\sqrt{\lambda \mu \tau(t - \tau)}$ and $I_0(\cdot)$ and $I_1(\cdot)$ are modified Bessel functions. Note that $\tau = x/v$ is not simply a convenient scaling of the x coordinate, but τ also represents the residence time in the free phase. The expressions h_{ij} represent the probability densities of the free residence time for different phases and different initial states of the particles. The first index indicates the initial state of the particle and the second index indicates the state of the particles the pdf is referring to. The distributions are zero for $\tau < 0$ and $\tau > t$ ($x < 0$ and $x > vt$). The delta functions at $\tau = 0$ and $\tau = t$ (which in x-space corresponds to $x = 0$ and $x = vt$) represent exponentially decreasing pulses and can also be identified as the fractions
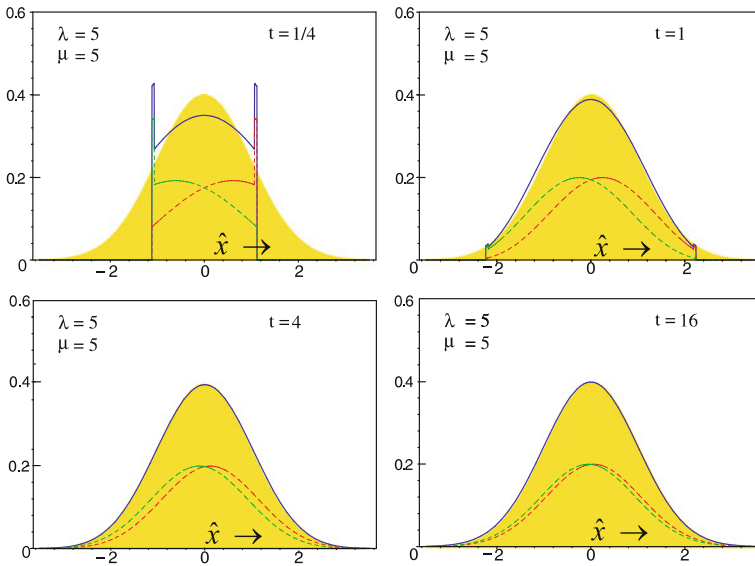
Fig. 2 Distributions of separate phases and total plume at 4 moments in time. Symmetric case ($\lambda = \mu$). Solid (*blue*) line for total plume. Dashed lines for (*green*) adsorbed phase and (*red*) free phase and *yellow* background for Gaussian distribution

of particles that, since $t = 0$, did not (yet) perform a change of state. In Figs. 2 and 3, we present graphs with the evolution in time of these distributions, using as initial condition the (unit) pulse consisting of free and adsorbed particles in equilibrium. Let π_f and π_a be the initial amount of particles in each phase. Equilibrium exists for $\frac{\pi_f}{\pi_a} = \frac{\mu}{\lambda}$, and, if the total amount is unity, we have:

$$\pi_a = \frac{\mu}{\lambda + \mu}; \quad \pi_f = \frac{\lambda}{\lambda + \mu}. \tag{23}$$

Thus, for $t = 0$:

$$N_f(x, t) = \pi_f \delta(x); \quad N_a(x, t) = \pi_a \delta(x).$$

We denote the residence distributions due to this initial condition as h_f^{eq} and h_a^{eq}:

$$\begin{aligned} h_f^{eq}(\tau, t) &= \pi_f h_{ff}(\tau, t) + \pi_a h_{af}(\tau, t) \\ h_a^{eq}(\tau, t) &= \pi_f h_{fa}(\tau, t) + \pi_a h_{aa}(\tau, t), \end{aligned} \tag{24}$$

while for the total amount of particles we have, $h_{tot}^{eq} = h_f^{eq} + h_a^{eq}$.

In Figs. 2 and 3, we compare distributions (24) and h_{tot}^{eq} with a Gaussian distribution with mean v^*t and variance $2D^*t$ representing the distribution of a solute with velocity v^* and dispersion D^*. All distributions are plotted versus a scaled variable $\hat{x}$:

$$\hat{x} = \frac{x - v^*t}{\sqrt{2D^*t}}. \tag{25}$$

Several stages of the system are shown. At early times ($t = 1/4$, Fig. 2, upper left graph) the pulses of free and adsorbed mass are still distinguishable. The pulses move apart in $\hat{x}$ space and are damped. The mass that 'leaves' the pulses gradually fills the space in between
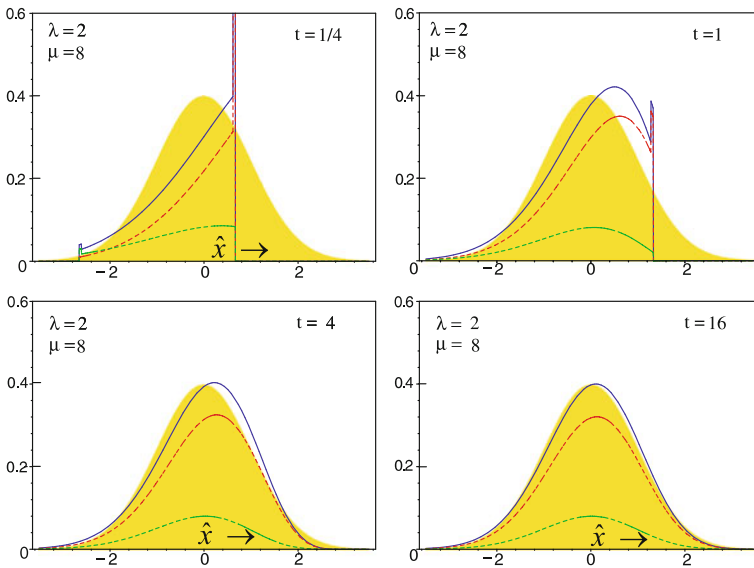
Fig. 3 Distributions of separate phases and total plume at 4 moments in time. Asymmetric case ($\lambda \neq \mu$). Solid (*blue*) line for total plume. Dashed lines for (*green*) adsorbed phase and (*red*) free phase and *yellow* background for Gaussian distribution

and builds up a distribution that becomes Gaussian in the end (e.g., $t = 16$, Fig. 2, lower right graph). The distribution in the interval between the pulses is absent in a pure wave system and is typical for the telegraph equation. In the final stage, the pulses are completely damped and the distribution approaches the normal distribution. Summarized, at early times the 'wave-character' dominates, at large times the 'diffusion-character' dominates, while at intermediate times the system is adequately described by a telegraph equation (traveling and dampened pulses + mixed zone in between). For $\lambda = \mu$ the Gaussian distribution is reached slightly faster than in the asymmetric case ($\lambda \neq \mu$), as seen in Fig. 3. For both cases, the pulses disappear for t exceeding both $3/\lambda$ and $3/\mu$. In the next section, local dispersion is included. We show that the two-dimensional distribution still may deviate from two-dimensional Gaussian functions even though the corresponding one-dimensional distribution is close to Gaussian.

4 Giddings–Eyring Model Including Dispersion

We extend the Giddings–Eyring model by including longitudinal and transverse dispersion. This way we obtain the following two-dimensional system.

$$\frac{\partial N_f}{\partial t} - D_L \frac{\partial^2 N_f}{\partial x^2} - D_T \frac{\partial^2 N_f}{\partial y^2} + v \frac{\partial N_f}{\partial x} = \mu N_a - \lambda N_f$$

$$\frac{\partial N_a}{\partial t} = \lambda N_f - \mu N_a, \tag{26}$$

where now N_f and N_a represent a two-dimensional particle density distribution $[L^{-2}]$ and D_L and D_T are the longitudinal and transverse dispersion coefficients. We do not use

different notations for the one- and two-dimensional particle densities. We assume that their distinction will be clear from the context.

It appears that the effect of transverse dispersion is much more dramatic than that of longitudinal dispersion, while its solution is much easier to derive. Therefore, we analyze longitudinal and transverse dispersion separately and start by including transverse dispersion first.

4.1 Transverse Dispersion

We use an approach proposed by Van Kooten (1996). Consider two distinct species, an adsorbing species (A) and a non-adsorbing (NA). Let the spatial distribution of the non-adsorbing species be given by $c_{NA}(x, y, t)$. Further, let τ be the 'free residence time' of the adsorbing particles and let the distribution of τ at time t be $h_{ij}(\tau, t)$, i.e. for particles in phase j with an initial unit pulse in phase i (see (22)). If the initial pulse in phase i is N_i^0, then at time t the amount of particles with free residence time between τ and $\tau + d\tau$ becomes $N_i^0 h_{ij}(\tau, t) d\tau$, where $\tau < t$. The spatial distribution of this fraction, $dN_{ij}(x, y, t)$, is equal to that of the non-adsorbing particles at $t = \tau$, or $c_{NA}(x, y, \tau)$. Summation over τ for of these fractions for τ, $0 \leq \tau \leq t$ gives:

$$N_{ij}(x, y, t) = N_i^0 \int_0^t h_{ij}(\tau, t) c_{NA}(x, y, \tau) \, d\tau. \tag{27}$$

We apply Van Kooten's approach first to the case with only transverse dispersion. For a non-adsorbing solute with advection in the x direction and dispersion in the y direction (D_L is assumed zero), the distribution is:

$$c_{NA}(x, y, t) = \frac{1}{2\sqrt{\pi D_T t}} \exp\left(-\frac{y^2}{4D_T t}\right) \delta(x - vt).$$

Insert this function in the integral (27). Because of the delta function, the integral can be evaluated directly. After substitution of τ by x/v, we obtain:

$$N_{ij}(x, y, t) = N_i^0 \frac{h_{ij}(\frac{x}{v}, t)}{2\sqrt{\pi D_T \frac{x}{v}}} \exp\left(-\frac{y^2}{4D_T \frac{x}{v}}\right). \tag{28}$$

For a fixed value of x, expression (28) describes the distribution in y direction of a certain amount of particles. The amount is equal to $N_i^0 h_{ij}(\frac{x}{v}, t)$ per unit of length in x direction and it spreads in the y direction as a Gaussian distribution with variance $2D_T \frac{x}{v}$. The transverse variance now depends on the x coordinate, which is clearly in conflict with a 2D Gaussian distribution. The interdependence of transverse variance and x coordinate can be understood by considering the residence times in the free phase. During the 'free phase', time particles travel in positive x direction and simultaneously spread in the y direction. At a given time t, the particles that have spent more time in the free phase are found further along the x direction. They are also more widely spread in y direction, since they have been subject to dispersion for a longer time. Further, note that for $\frac{x}{v>t}$, the functions $h_{ij}(\frac{x}{v}, t)$ are zero. Therefore, $N_{ij}(x, y, t)$ is zero for $x > vt$.

In Fig. 4, this is illustrated by 2D contours for unit initial pulses in the free and adsorbed phase. The following scaled coordinates are used:

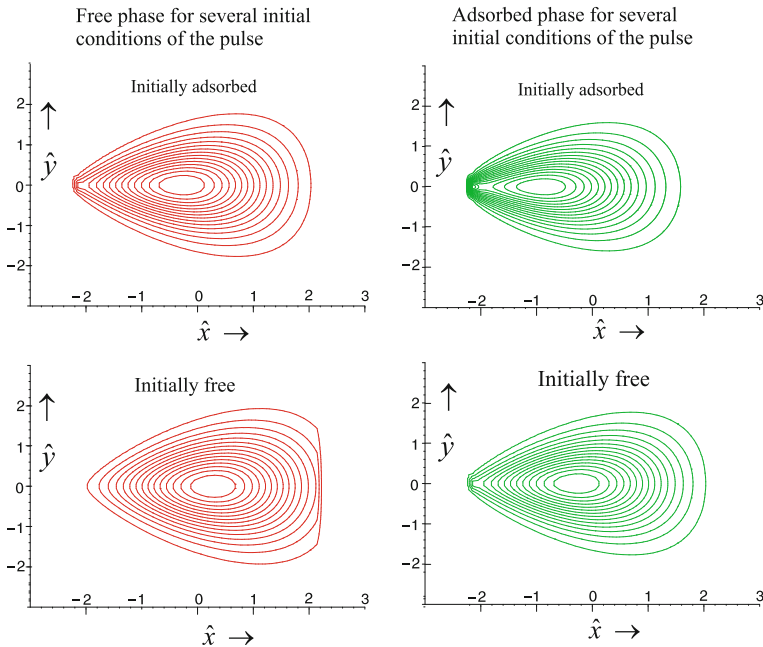$$\hat{x} = \frac{x - v^* t}{\sqrt{2D^* t}}; \quad \hat{y} = \frac{y}{\sqrt{2D_T t}}. \tag{29}$$

Fig. 4 Contour-lines for free phase (*red*) and adsorbed phase (*green*) for several initial conditions. The symmetric case ($\lambda = 5$ and $\mu = 5$) at time $t = 1$

For a Gaussian distribution with dispersion coefficients D^* and D_T/R in the longitudinal and transverse direction one would expect elliptic contour-lines. Figure 4, however, shows typical 'cigar-shaped' contours. It is clear that close to the original injection point (in Fig. 4 around $\hat{x} = -2$) the particles have spend a relatively short time, τ, in the 'free' phase. During this time, not only the particles displace very little in longitudinal direction, but also the spread in transverse direction is very limited. The result of this is that x displacement and y-spread are no longer independent, which is in contradiction to a truly Gaussian system. Also note that in the 1D case in Fig. 2 the same parameters have been used and the corresponding distribution in x direction comes out almost as a Gaussian curve (Fig. 2, upper right graph).

4.2 Longitudinal and Transverse Dispersion

Analytical solutions including longitudinal and transverse dispersion have been obtained by Carnahan and Remer (1984), but not in a closed-form. The integral expression by Carnahan is, in essence, equal to the one obtained by Van Kooten's approach:

$$N_{ij}(x, y, t) = \frac{N_i^0}{\sqrt{D_L D_T}} \int_0^t \frac{h_{ij}(\tau, t)}{4\pi\tau} e^{-\frac{(x-v\tau)^2}{4D_L\tau} - \frac{y^2}{4D_T\tau}} \, d\tau \tag{30}$$

We apply expression (30) to evaluate the 'full' system (i.e, including advection, dispersion and sorption) using the following values: $\lambda = 0.2$, $\mu = 0.2$, $v = 1$, $D_L = 0.5$ and $D_T = 0.1$. The kinetics-induced dispersion coefficient D^* now becomes 0.62, which is in the same order of magnitude as D_L.
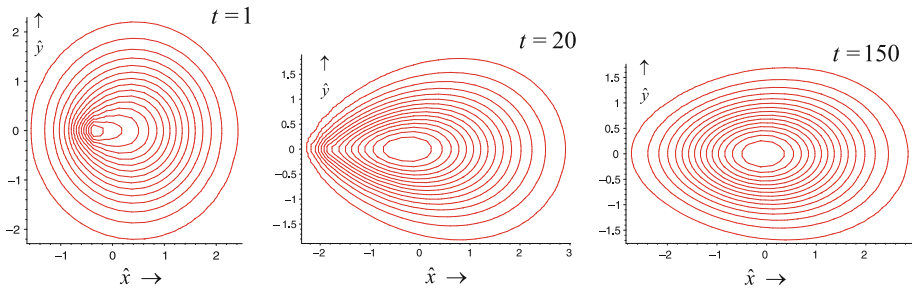
Fig. 5 Full two-dimensional case. Distribution of the free phase at various times for an initial pulse in equilibrium; symmetric $\lambda = 0.2$ and $\mu = 0.2$; $D_L = 0.5$; $D_T = 0.1$; $v = 1$

The contour-lines in Fig. 5 represent the distribution of the free phase for $t = 1$, $t = 20$ and $t = 150$, for the case of an initial pulse in equilibrium. Note that for longitudinal and transverse coordinates, we have applied the same scaling as in Fig. 4, (see (29)). At a short time ($t = 1$), almost circular contours occur, which suggests Gaussianity. At this stage, microdispersion dominates the spreading process, which now progresses in a Gaussian way. At an intermediate time ($t = 20$), the 'cigar-shaped' contours start to develop. Here, we observe an increasing influence of the non-Gaussian kinetics-induced dispersion. Finally, at large times ($t = 150$), the distribution becomes Gaussian again, with elliptic contours. The parameters of the early and late Gaussian distribution are quite different. For short times, we have velocity v and dispersion coefficients D_L and D_T. For large times, the velocity becomes v^* and dispersion coefficients $D_L/R + D^*$ and D_T/R for the longitudinal and transverse direction, respectively. The early Gaussian distribution occurs because directly after the start of the pulse the effect of kinetic exchange between the phases is still small and the free phase consists mainly of particles that did not yet change their state. Therefore, they behave as a non-adsorbing solute. As time goes on the influence of kinetics becomes more apparent and 'cigar-shaped' contours develop.

5 Moment Analysis

5.1 One-Dimensional

Analysis of spatial moments and their development in time has been has been frequently used in the literature to illustrate Gaussian and non-Gaussian features of transport processes. The method was introduced by Aris (1956), while studying the flow of solutes through a capillary tube (Taylor dispersion). Later, it was successfully applied to solute transport in a layered porous medium in Marle et al. (1967). Recently, in the literature, there is a growing interest for temporal moments of breakthrough curves, e.g. see Lawrence et al. (2002) and Sanchez-Vila and Rubin (2003). In our paper, however, we focus only on the analysis of the spatial moments. For contaminant transport with sorption, spatial moment analysis was applied by Valocchi (1988), Valocchi and Quinodoz (1989), Chrysikopoulos et al. (1992) and Souadnia et al. (2002). These authors examine the asymptotic values of zero, first and second moments. Solutions for the entire pre-asymptotic regime of zeroth, first and second moments are derived by Michalak and Kitanidis (2000). However, one of their expressions for the central second moment turns out to be incorrect. We copy here the formula (the ⊕ is

a +, but should be a −) from Michalak and Kitanidis (2000), page 2136 for the normalized central moment, where the solute is in the free phase at time 0 *and* at time t:

$$
\sigma_{ff}^2 = \frac{t^2 A v^2 \beta \, (\beta - 1)^2}{(\beta + 1)^2 (1 + \beta A)^2} + t \left(\frac{2D}{\beta + 1} + \frac{2 v^2 \beta}{k (\beta + 1)^3} \right)
$$
$$
+ t A \left(\frac{4 v^2 \beta \, (-\beta^2 A - \beta^2 - \beta + 1)}{k (1 + \beta A)^2 (\beta + 1)^3} \right) + t A \left(\frac{2 D \beta \, (\beta - 1)}{(\beta + 1)(1 + \beta A)} \right)
$$
$$
+ \frac{2 v^2 \beta \, (1 - A) \, (3 \beta^2 A - 3 - \beta \, (A \oplus 1))}{k^2 (1 + \beta A)^2 (\beta + 1)^4} + \frac{4 D \beta \, (1 - A)}{k (1 + \beta A)(\beta + 1)^2}. \tag{31}
$$

Here, Michalak and Kitanidis abbreviate $A = A(t) = \exp(-(\beta + 1)kt)$ and use the notation

$$
k = \mu, \quad \beta = \lambda / \mu.
$$

By giving the expressions for σ_{ff}^2, σ_{fa}^2, σ_{af}^2 and σ_{aa}^2, Michalak and Kitanides suggest that these expressions may be used to obtain variances for a general initial condition, by linearity. However, such a superposition can only be composed for the non-centralized moments. At large times, the first and second moments appear to increase at a constant rate, which suggest that there exist an effective velocity v_e and effective dispersion coefficient D_e:

$$
v_e = \frac{\mu}{\lambda + \mu} v \quad D_e = \frac{\lambda \mu}{(\lambda + \mu)^3} v^2 + \frac{\mu}{\lambda + \mu} D. \tag{32}
$$

5.2 Two-Dimensional

The 2D case is described by the Eq. (26). We may distinguish two different types of moments. The first type is that of the marginal moments, or moments with respect to the x coordinate ignoring the information on the y coordinates of the particles. The second type consists of conditional moments, either a moment with respect to x for a given value of y or a moment with respect to the y for a given value of x. Interestingly, the marginal moments for the 2D case are identical to the moments for the 1D case. In the following subsections, we discuss the conditional moments.

5.2.1 The x-Moments Conditioned On y

This category of moments represents expected values of x^n for a population of particles with a specific y coordinate. Note that these moments are a function of y. We define these moments as:

$$
M_f^{(n)}(y) = \int_{-\infty}^{+\infty} x^n N_f(x, y) \, dx, \quad M_a^{(n)}(y) = \int_{-\infty}^{+\infty} x^n N_a(x, y) \, dx
$$

For $n = 0$ the expressions represent for each phase the particle distribution along the y direction (the total mass of particles with the specified y coordinate). Note that the higher-order moments ($n > 0$) are not yet divided by the zeroth moment, so higher-order moments are not normalized. For the initial condition, we consider a (unit) pulse with the phases in equilibrium. Then, the two-dimensional particle distribution becomes:

$$
N_i^{eq}(x, y) = \int_0^t h_i^{eq}(\tau, t) \frac{e^{-\frac{(x - v\tau)^2}{4 D_L \tau} - \frac{y^2}{4 D_T \tau}}}{4 \pi \tau \sqrt{D_L D_T}} \, d\tau \tag{33}
$$

where i is a or f. This expression is obtained by applying (30), replacing h_{ij} by h_i^{eq} (see (24)) and taking N_i^0 equal to 1. For the equilibrium initial condition the moments are:

$$M_i^{(n)}(y) = \int\limits_{-\infty}^{+\infty} x^n N_i^{eq}(x, y)\, dx$$

When we use (33) and change the order of integration, the zeroth, first and second moments become:

$$M_i^{(0)}(y) = \int\limits_0^t h_i^{eq}(\tau, t) \frac{e^{-\frac{y^2}{4D_T\tau}}}{2\sqrt{\pi D_T\,\tau}}\, d\tau \tag{34}$$

$$M_i^{(1)}(y) = \int\limits_0^t v\tau\, h_i^{eq}(\tau, t) \frac{e^{-\frac{y^2}{4D_T\tau}}}{2\sqrt{\pi D_T\,\tau}}\, d\tau \tag{35}$$

$$M_i^{(2)}(y) = \int\limits_0^t (2D_L\tau + v^2\tau^2) h_i^{eq}(\tau, t) \frac{e^{-\frac{y^2}{4D_T\tau}}}{2\sqrt{\pi D_T\,\tau}}\, d\tau. \tag{36}$$

Figure 6 shows the distribution along the y-axis for the zeroth moments of free and adsorbed phase for several times. The initial condition here is the equilibrium situation. The zeroth moment is plotted horizontally. The figure shows that particles of both phases gradually spread out in y direction. Note in the figure at the right-hand side that at $t = 5$ the adsorbed phase is concentrated along $y = 0$ and the curve has a pulse-shaped component $\delta(y)$ for $y = 0$. This pulse represents the particles that did not yet spend time in the free phase and are still in the initial position. At larger times, most adsorbed particles do have spent time in the free phase and the spreading in y direction becomes visible.

Figure 7 shows the first moment for the free phase. The first moment, plotted horizontally, can be interpreted as the average distance travelled in the x direction for the particles with a specific y coordinate. As it appears, for $y = 0$, the first moments are smaller than for values of y greater or smaller than 0. It is an alternative illustration of the tailing effect. Particles spending less time in the free phase have less opportunity to displace in the x direction and spread in the y direction. Thus, a considerable fraction of these particles are found around the point of origin. Further away from the y-axis, particles occur that have been able to disperse laterally. Therefore, they did spend some time in the free phase and, consequently, were also displaced further along the x-axis. Once more, we conclude that displacements in x and y directions are mutually dependent. This dependence in the spreading pattern is non-Gaussian.

5.2.2 The y-Moments, Conditioned On x

The y-moments conditioned on x are defined as:

$$M_f^{(m)}(x) = \int\limits_{-\infty}^{\infty} y^m N_f(x, y)\, dy, \quad M_a^{(m)}(x) = \int\limits_{-\infty}^{\infty} y^m N_a(x, y)\, dy,$$

We analyze the y-moments by the Laplace transform using the following initial conditions:

$$N_f(x, y, t)\big|_{t=0} = \pi_f \delta(x)\delta(y) \quad N_a(x, y, t)\big|_{t=0} = \pi_a \delta(x)\delta(y).$$
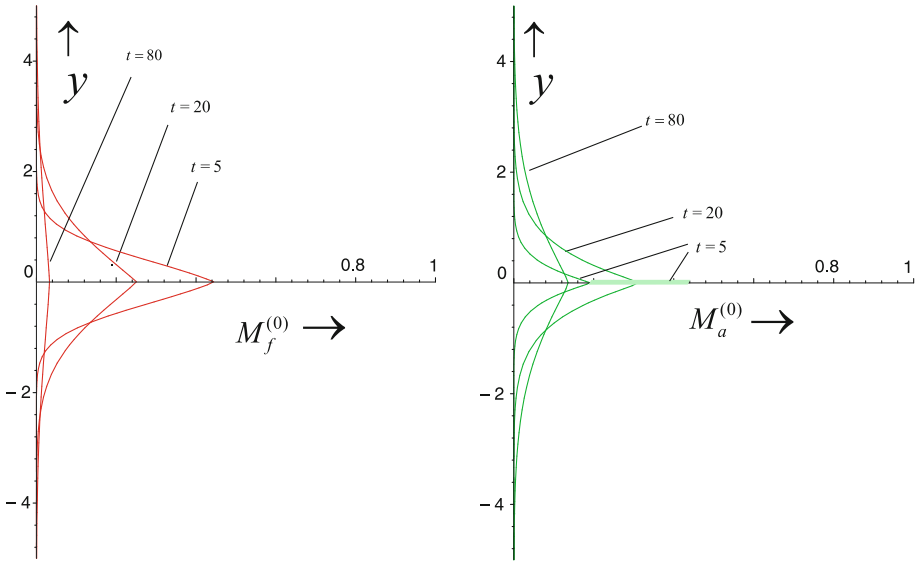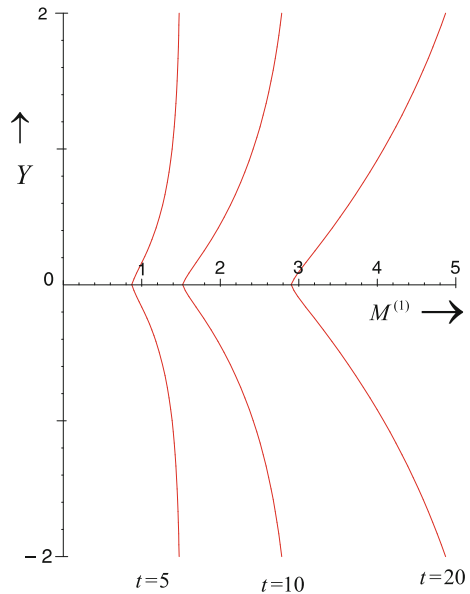
Fig. 6 Zeroth moments as given by (34) versus y for $t = 5, 20, 80$, *left* free phase, *right* adsorbed phase; $\lambda = \mu = 0.05$; $D_T = 0.03$. Zeroth moment on the horizontal axis. In the figure at the *right*-hand side, the curve for $t = 5$ has a pulse-shaped component $\delta(y)$ at $y = 0$

Fig. 7 First moments for free phase versus y from (35) for $t = 5, 10, 20$. Numerical values: $\lambda = 0.05$; $\mu = 0.05$; $v = 0.3$; $D_L = 0.3$; $D_T = 0.03$. First moment on the horizontal axis

After applying the Laplace transform to Eq. (26) and eliminating the transform of N_a, we obtain the following differential equation:

$$D_L \frac{\partial^2 \widehat{N}_f}{\partial x^2} + D_T \frac{\partial^2 \widehat{N}_f}{\partial y^2} - v \frac{\partial \widehat{N}_f}{\partial x} - sb\widehat{N}_f + b\pi_f \delta(x)\delta(y) = 0,$$

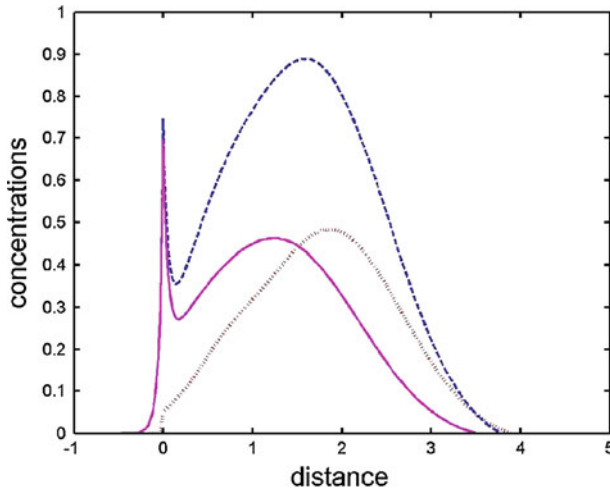**Fig. 8** Zeroth moment for total concentration $M^{(0)}$ (*dashed*), free concentration $M_f^{(0)}$ (*dotted*) and adsorbed $M_a^{(0)}$ concentration (*drawn*). Small numerical inaccuracies lead to the fact that the zeroth moment for the total concentration is below the curve for the free concentration. The peaks at $x = 0$ representing the function $\delta(x)$ are "approximated" by two exponential curves for reasons of illustration

where $\widehat{N}_f$ denotes the particle density in Laplace space, s is the Laplace parameter and b is an expression depending on s:

$$b = \frac{s + \lambda + \mu}{s + \mu}$$

$\widehat{N}_a$ is related to $\widehat{N}_f$ by (see Eq. (26)):

$$(s + \mu)\widehat{N}_a - \pi_a \delta(x)\delta(y) = \lambda \widehat{N}_f$$

After taking the moments with respect to y, we find for the zeroth moment:

$$D_L \frac{\partial^2 \widehat{M}_f^{(0)}}{\partial x^2} - v \frac{\partial \widehat{M}_f^{(0)}}{\partial x} - sb\widehat{M}_f^{(0)} + b\pi_f \delta(x) = 0$$

$$\widehat{M}_a^{(0)} = \frac{\lambda}{s + \mu}\widehat{M}_f^{(0)} + \frac{\pi_a}{s + \mu}\delta(x)$$

The solution for $\widehat{M}_f^{(0)} = \widehat{M}_f^{(0)}(x)$ is

$$\widehat{M}_f^{(0)} = \frac{b\pi_f}{\sqrt{v^2 + 4bs D_L}} \exp\left(\frac{xv - |x|\sqrt{v^2 + 4bs D_L}}{2D_L}\right)$$

where we use that the concentrations are zero at $x = \pm\infty$. The inverse can be found with numerical Laplace inversion algorithms (Davies and Martin 1979; Stehfest 1970; Abate and Valkó 2004) and is shown in Fig. 8.

For the second moment, we obtain the equations:

$$D_L \frac{\partial^2 \widehat{M}_f^{(2)}}{\partial x^2} - v \frac{\partial \widehat{M}_f^{(2)}}{\partial x} - sb\widehat{M}_f^{(2)} + 2D_T \widehat{M}_f^{(0)} = 0$$

$$s\widehat{M}_a^{(2)} = \lambda\widehat{M}_f^{(2)} - \mu\widehat{M}_a^{(2)}$$

where we use that

$$\int_{-\infty}^{\infty} y^2 \frac{\partial^2 \widehat{N}_f}{\partial y^2} \, \mathrm{d}y = \widehat{M}_f^{(0)}.$$

with the solution (for $x > 0$):

$$\widehat{M}_f^{(2)}(x) = b\pi_f \frac{\mu^2 D_L}{\lambda + \mu} \frac{\exp\left(\frac{xv - x\sqrt{v^2 + 4bsD_L}}{2D_L}\right)}{v^2 + 4bsD_L} \times \frac{\mu}{v}\left(x + \frac{2D_L}{\sqrt{v^2 + 4bsD_L}}\right),$$

$$\widehat{M}_a^{(2)}(x) = \frac{\lambda}{s + \mu} \widehat{M}_f^{(2)}(x).$$

The ratio of the numerically (Stehfest 1970) inverted $\widehat{M}_f^{(2)}$ and $\widehat{M}_f^{(0)}$ is the normalized and centralized second moment (conditioned on x) and this ratio turns out to be x/Pe. Thus, the lateral spread depends on x, which (again) explains the tailing and the previously observed 'cigar shape'.

6 Conclusions

We discuss a stochastic particle approach, considering a particle that changes between a mobile and immobile state governed by a Markov chain, while its spatial displacement is governed by a random walk. Our analysis shows that it is possible to derive the correct set of differential equations from a stochastic model for a single particle.

To examine the non-Gaussian nature of the spreading process, we analyze first the telegrapher's equation. This equation arises when only advection and kinetic sorption is considered. We show that in such a system an apparent dispersion process occurs, generated only by the kinetic changing of the particle in states with different velocities (i.e. *zero* or v). This 'kinetics-induced' dispersion is non-Gaussian for short and intermediate times, while at large times the process develops as Gaussian dispersion. When hydrodynamic dispersion is included again, the spreading process becomes a combination of a Gaussian and non-Gaussian dispersion. We illustrate this for the 2D case. At short times, the process is Gaussian, since hydrodynamic dispersion is the dominating process. At intermediate times, the influence of kinetic-induced dispersion increases and the spreading becomes non-Gaussian. Finally, at large times, the dispersion becomes Gaussian again, but the (effective) longitudinal dispersion coefficient has an additional term due to the kinetics. Moreover, we find for the 2D case that the transverse spreading depends on the longitudinal coordinate, resulting in 'cigar-shaped' contours. The mechanism is best illustrated when longitudinal dispersion is assumed zero. Here, the particles displace in the x direction by advection and spread transversely by dispersion. Particles spending more time in the adsorbed phase are displaced less in x direction and also less spread out in y direction. In a truly Gaussian distribution, the transverse spreading is independent of the longitudinal coordinate. When longitudinal dispersion is included the same effect is observed, although for short times (compared to the kinetic exchange rate) the situation is now dominated by hydrodynamic dispersion. With respect of the validity of effective properties (velocity and dispersion), we conclude the following. The velocity and dispersion coefficients are represented by the rate of increase in the first and centralized second moments (times $1/2$). For cases with low adsorption and desorption rates, the rates of increase for the moments remain time dependent for a relatively longtime. We conclude

that even for a homogeneous medium constant effective properties cannot be defined directly after the start of solute injection. For large times, an asymptotic behavior is observed with a constant mean displacement and rate of dispersion, while the third moment vanishes and the kurtosis approaches a value of 3. This can be proved via our stochastic model by applying a sophisticated version of the central limit theorem (Sect. 2.2). The critical time, required before dispersion coefficients becomes constant, is in the order of $3/(\lambda + \mu)$. The effective velocity is $v\mu/(\lambda + \mu)$, exactly as in the case of linear equilibrium adsorption. However, at early times, the free particles move with the original groundwater velocity and build up a lead with respect to the adsorbed phase. In the asymptotic stage, the adsorbed and free particles displace with the same average velocity, but the lead of the free plume is maintained. The effective longitudinal dispersion can be much higher than in the case of linear equilibrium adsorption. The additional term $v^2\lambda\mu/(\lambda + \mu)^3$ depends also on the groundwater velocity. It is remarkable that it depends on v^2, while the microscale dispersion is linear in v.

References

Abate, J.J., Valkó, P.P.: Multi-precision Laplace transform inversion. Int. J. Numer. Methods Eng. **1**(60), 979–993 (2004)

Aris, R.: On the dispersion of a solute in a fluid flowing through a tube. Proc. R Soc. Lond. Ser. A **235**, 67–77 (1956)

Attinger, S., Dentz, M., Kinzelbach, H., Kinzelbach, W.: Temporal behaviour of a solute cloud in a chemically heterogeneous porous medium. J. Fluid Mech. **386**, 77–104 (1999)

Barenblatt, G., Zheltov, I., Kochina, I.: Basic concepts in the theory of seepage of homogeneous liquids in fissured rocks [strata]. J. Appl. Math. Mech. **24**(5), 1286–1303 (1960)

Benson, D.A. Meerschaert, M.M.: A simple and efficient random walk solution of multi-rate mobile/immobile mass transport equations. Adv. Water Resour. **32**(4), 532–539 (2009) doi:10.1016/j.advwatres.2009.01.002

Berkowitz, B., Cortis, A., Dentz, M., Scher, H.: Modeling non-Fickian transport in geological formations as a continuous time random walk. Rev. Geophys. **44**(2) (2006) doi:10.1029/2005RG000178

Biggar, J.W., Nielsen, D.R.: Miscible displacement: 11 behaviour of tracers. Soil Sci. Soc. Am. Proc. **26**, 125–128 (1962)

Bouchaud, J.P., Georges, A.: Anomalous diffusion in disordered media: statistical mechanisms, models and physical applications. Phys. Rep. **195**(4–5), 127–293 (1990) doi:10.1016/0370-1573(90)90099-N

Carnahan, C., Remer, J.: Nonequilibrium and equilibrium sorption with a linear sorption isotherm during mass transport through an infinite porous medium: some analytical solutions. J. Hydrol. **73**, 227–258 (1984)

Carrera, J., Sánchez-Vila, X., Benet, I., Medina, A., Galarza, G., Guimerà, J.: On matrix diffusion: formulations, solution methods and qualitative effects. Hydrogeol. J. **6**(1), 178–190 (1998)

Chandramouli, R.: Continuous-time sequential decision feedback: revisited. In: 2002 Conference on Information Sciences and Systems, Princeton University, Princeton, March 20–22, 2002

Chrysikopoulos, C.V., Kitanidis, P.K., Roberts, P.V.: Generalized Taylor-Aris moment analysis of the transport of sorbing solutes through porous media with spatially periodic retardation factors. Transp. Porous Media **7**, 163–185 (1992)

Coats, K., Smith, B.: Dead-end pore volume and dispersion in porous media. Old SPE J. **4**(1), 73–84 (1964)

Dagan, G.: Time-dependent macrodispersion for solute transport in anisotropic heterogeneous aquifers. Water Resour. Res. **24**(9), 1491–1500 (1988)

Davies, B., Martin, B.: Numerical inversion of the Laplace transform: a survey and comparison of methods. J. Comput. Phys. **33**(1), 1–32 (1979)

De Smedt, F., Wierenga, P.: Mass transfer in porous media with immobile water. J. Hydrol. **41**(1–2), 59–67 (1979)

Dehling, H.G., Hoffmann, A.C., Stuut, H.W.: Stochastic models for transport in a fluidized bed. SIAM J. Appl. Math. **60**(1), 337–358 (electronic) (2000)

Dekking, M., Kong, D.: Multimodality of the Markov binomial distribution. J. App. Probab. arXiv:1102.3613. (2011a) (to appear)

Dekking, M., Kong, D.: A simple stochastic reactive transport model, arXiv:1106.2912. Submitted (2011b)

Delay, F., Ackerer, P., Danquigny, C.: Simulating solute transport in porous or fractured formations using random walk particle tracking: a review. Vadose Zone J. (4), 360–379 (2005) doi:10.2136/vzj2004.0125

Dentz, M., Berkowitz, B.: Transport behavior of a passive solute in continuous time random walks and multirate mass transfer. Water Resour. Res. **39**(5) (2003) doi:10.1029/2001WR001163

Dentz, M., Bolster, D.: Distribution-versus correlation-induced anomalous transport in quenched random velocity fields. Phys. Rev. Lett. **105**(24) (2010) doi:10.1103/PhysRevLett.105.244301

Dentz, M., Castro, A.: Effective transport dynamics in porous media with heterogeneous retardation properties. Geophys. Res. Lett. **36** (2009) doi:10.1029/2008GL036846

Dentz,M. Cortis, A. Scher, H. Berkowitz, B.: Time behavior of solute transport in heterogeneous media: transition from anomalous to normal transport. Adv. Water Resour. **27**(2) 155–173 (2004) doi:10.1016/j.advwatres.2003.11.002

Dentz, M., Tartakovsky, D.M.: Delay mechanisms of non-Fickian transport in heterogeneous media. Geophys. Res. Lett. **33**(24) (2006) doi:10.1029/2006GR027054

Dieulin, A., Matheron, G., De Marsily, G.: Growth of the dispersion coefficient with mean travelled distance in porous media. Sci. Total Environ. **21**, 319–328 (1981)

Dieulin, A., Matheron, G., De Marsily, G., Beaudoin, B.: Time dependence of an 'equivalent dispersion coefficient' for transport in porous media. In: Proceedings Euromech Symposium (1981b)

Feller, W.: An Introduction to Probability Theory and its Applications, vol. 2. 2nd edn. Wiley, New York (1971)

Fürth, R.: Die Brownsche bewegung bei berücksichtigung einer persistenz der bewegungsrichtung. Z Phys. **2**, 244–256 (1920)

Gelhar, L.W., Gutjahr, A.L., Naff, R.: Stochastic analysis of macrodispersion in a stratified aquifer. Water Resour. Res. **15**(6), 1387–1397 (1979)

Giddings, J.C.: Kinetic origin of tailing in chromotography. Anal. Chem. **35**(13), 1999–2002 (1963)

Giddings, J.C., Eyring, H.: A molecular dynamic theory of chromotography. J. Phys. Chem. **59**, 416–421 (1955)

Goldstein, S.: On diffusion by discontinuous movements, and on the telegraph equation. Quart. J. Mech. Appl. Math. **4**, 129–156 (1951)

Gut, A., Ahlberg, P.: On the theory of chromatography based upon renewal theory and a central limit theorem for randomly iterated indexed partial sums of random variables. Chem. Scr. **18**(5), 248–255 (1981)

Haggerty, R., Gorelick, S.: Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity. Water Resour Res. **31**(10), 2383–2400 (1995)

Haggerty, R., Harvey, C., Schwerin, C.von , Meigs, L.: What controls the apparent timescale of solute mass transfer in aquifers and soils? A comparison of experimental results. Water Resour. Res. **40**(1), W01,510 (2004)

Haggerty, R., McKenna, S., Meigs, L.: On the late-time behavior of tracer test breakthrough curves. Water Resour. Res. **36**(12), 3467–3479 (2000)

Harvey, C., Gorelick, S.: Temporal moment-generating equations: modeling transport and mass transfer in heterogeneous aquifers. Water Resour. Res. **31**(8), 1895–1911 (1995)

Hillel, T.: Nichtlineare hyperbolische systeme zur modellierung von ausbreitungsvorgängen und anwendung auf das Turing modell. Ph.D. thesis, Universität Tübingen (1995)

Kac, M.: A stochastic model related to the telegrapher's equation. Rocky Mt. J. Math. **4**, 487–509 (1956)

Keller, R.A., Giddings, J.C.: Multiple zones and spots in chromatography. J. Chromatogr. **3**, 205–220 (1960)

Lassey, K.: Unidimensional solute transport incorporating equilibrium and rate limited isotherms with first order loss. 1 Model conceptualizations and analytical solutions. Water Resour. Res. **24**(3), 343–350 (1988)

Lawrence, A., Sanchez-Vila, X., Rubin, Y.: Conditional moments of the breakthrough curves of kinetically sorbing solute in heterogeneous porous media using multirate mass transfer models for sorption and desorption. Water Resour. Res. **38**(11) (2002) doi:10.1029/2001WR001006

Maloszewski, P., Zuber, A.: On the calibration and validation of mathematical models for the interpretation of trace experiments in groundwater. Adv. Water Resour. **15**, 47–62 (1992)

Margolin, G. Dentz, M. Berkowitz, B.: Continuous time random walk and multirate mass transfer modeling of sorption. Chem. Phys. **295**(1) 71–80 (2003) doi:10.1016/j.chemphys.2003.08.007

Marle, C., Simandoux, P., Pacsirszky, J., Gaulie, C.: Étude du déplacement de fluides miscibles en milieu poreux stratifié. Rev. Inst. Fr. du Pétrole **12**(2), 272–294 (1967)

Masoliver, J., Weiss, G.H.: Finite-velocity diffusion. Eur. J. Phys. **17**, 190–196 (1996)

Michalak, A., Kitanidis, P.K.: Macroscopic behavior and random-walk particle tracking of kinetically sorbing solutes. Water Resour. Res. **36**(8), 2133–2146 (2000)

Mishra, A., Gutjahr, A., Rajaram, H.: Transport with spatially variable kinetic sorption: recursion formulation. Adv. Water Resour. **22**(5), 549–555 (1999)

Montroll, E.W., Weiss, G.: Random walks on lattices ii. J. Math. Phys. **6**, 167–181 (1965)

Neuman, S.P., Winter, C.L., Neuman, C.M.: Stochastic theory of field scale Fickian dispersion in anisotropic media. Water Resour. Res. **23**(3), 453–466 (1987)

Nkedi-Kizza, P., Biggar, J., Selim, H., Van Genuchten, M., Wierenga, P., Davidson, J., Nielsen, D.: On the equivalence of two conceptual models for describing ion exchange during transport through an aggregated oxisol. Water Resour. Res **20**(8), 1123–1130 (1984)

Ross, S.M.: Introduction to Probability Models. 7th edn. Harcourt/Academic Press, Burlington (2000)

Roth, K., Jury, W.: Linear transport models for adsorbing solutes. Water Resour. Res. **29**(4), 1195–1203 (1993)

Salamon, P., Fernandez-Garcia, D., Gomez-Hernandez, J.J.: Modeling mass transfer processes using random walk particle tracking. Adv. Water Resour. **42**(11) (2006) doi:10.1029/2006WR004927

Sanchez-Vila, X., Rubin, Y.: Travel time moments for sorbing solutes in heterogeneous domains under non-uniform flow conditions. Water Resour. Res. **39**(4) (2003) doi:10.1029/2002WR001399

Scheidegger, A.E.: An evaluation of the accuracy of the diffusivity equation for describing miscible displacement in porous media. In: Proceedings of Theory of Fluid Flow in Porous Media Conference. University of Oklahoma. pp. 101–116 (1959)

Schmidlin, F.: Theory of trap-controlled photo induction. Phys. Rev. B **16**(6), 2362–2385 (1977)

Schumer, R., Benson, D., Meerschaert, M., Baeumer, B.: Fractal mobile/immobile solute transport. Water Resour. Res. **39**(10) (2003) doi:10.1029/2003WR002141

Souadnia, A., Didierjean, S., Moyne, C.: Transient dispersion in porous media: a comparison between exact and approximate solutions in a case study. Trans. Porous Media **47**, 245–277(33) (2002)

Stehfest, H.: Algorithm 368, numerical inversion of the Laplace transforms. Commun. ACM **1**(13), 47 (1970)

Taylor, G.I.: Diffusion by discontinuous movements. Proc. Lond. Math. Soc. **20**, 196–212 (1920)

Valocchi, A.J.: Theoretical analysis of deviations from local equilibrium during sorbing solute transport through homogeneous idealized stratified aquifers. J. Contam. Hydrol. **2**, 191–207 (1988)

Valocchi, A.J., Quinodoz, H.A.M.: Application of the random walk method to simulate the transport of kinetically adsorbing solutes. In: Groundwater Contamination, IAHS Publications, vol. 185, pp. 35–42. IAHS (1989)

Van Genuchten, M., Wierenga, P.: Mass transfer studies in sorbing porous media: II. Experimental evaluation with tritium. Soil Sci. Soc. Am. J. **41**, 272–278 (1977)

Van Genuchten, M.T., Wierenga, P.: Mass transfer studies in sorbing porous media. I analytical solutions. Soil Sci. Soc. Am. J. **40**(4) (1976)

Van Genuchten, M.Th., Wierenga, P.J.: Mass transfer studies in sorbing porous media: I analytical solutions. Soil Sci. Soc. Am. J. **40**(4), 473–480 (1976)

Van Kooten, J.J.A.: A method to solve the advection-dispersion equation with a kinetic adsorption isotherm. Adv. Water Resour. **19**(4), 193–205 (1996)

Viveros, R., Balasubramanian, K., Balakrishnan, N.: Binomial and negative binomial analogues under correlated Bernoulli trials. Am. Stat. **48**, 243–247 (1994)

Weiss, G.H.: Aspects and Applications of the Random Walk. North Holland Press, Amsterdam (1994)

Weiss, G.H.: Some applications of persistent random walks and the Telegrapher's equation. Phys. A **311**, 381–410 (2002)