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Passage times of asymmetric anomalous walks with multiple paths

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Abstract

We investigate the transient and the long-time behaviour of asymmetric anomalous walks in heterogeneous media. Two types of disorder are worked out explicitly: weak and strong disorder; in addition, the occurrence of disordered multiple paths is considered. We calculate the first passage time distribution of the associated stochastic transport process. We discuss the occurrence of the crossover from a power law to an exponential decay for the long-time behaviour of the distribution of the first passage times of disordered biased walks.

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1. Introduction

The study of asymmetric random walks has been an important issue in understanding problems of hydrodynamics dispersion [1] in many areas of science such as the physics of fluids [2]. The concept of asymmetric walks [3, 4] applies also to geophysics [5–7], polymer physics [8, 9], ageing and glasses [1, 10, 11], etc.

It is known that the presence of bias drastically changes the properties of the random walks in random media [1]. In particular, depending on the type of the disorder [12] the bias breaks down possible perturbation theories to tackle random media problems [13]. A related complex problem is the analysis of the first passage time distribution (FPTD) in the presence of disorder [14] and bias. The presence of bias and disorder compete with each other leading to unexpected results [15]; the physical reason for this fact is the effect of the drift (bias) *against* the disorder (localization) [1, 8, 10, 16].

If the disorder strength is not so high there is not localization and therefore the disorder only introduces a renormalization in the kinetic coefficients. Thus we expect that the FPTD will not change drastically, so at long time, due to the drift, the decay of the FPTD will be controlled by an exponential decay factor e^{-Ct}, where the constant C is related to the bias. If the walks were *symmetric*, the long-time behaviour of the FPTD would just be given by the power law $\propto t^{-3/2}$. Therefore in non-symmetric weak-disordered walks if we consider a suitable time-scale we should see the crossover between the behaviours $t^{-3/2}$ to e^{-Ct}. Thus, the interesting point is to analyse the whole temporal behaviour of the FPTD in the presence of bias and disorder. Another important issue to understand is the transient anomalous hydrodynamics dispersion in heterogeneous systems, i.e., the finite-size effects in the presence of weak disorder. One of the goals of the present paper is to find the associated critical length in terms of the parameters that characterize the drift and the weak disorder [17].

If the disorder is strong enough the current of particles will eventually vanish; then at very long time we expect a power-law decay for the FPTD, with maybe some new exponent depending on the strength of the disorder. Nevertheless, in the intermediate-time regime, when the anomalous current is still non-null, it is not clear how the behaviour of the FPTD is influenced by the strength of the bias.

In the present paper, we consider all these interesting questions by using the continuous-time random walk (CTRW) approach, i.e., the Hartree approximation, to tackle problems of weak and strong disorders. In addition, we also consider the situation when there are stagnant volumes or dead ends in heterogeneous media. Therefore, a full analysis of the transport process is made by using a multiple path approach in the Hartree approximation, i.e., the transport is described in terms of a multistate CTRW process [17].

2. The propagator of the continuous-time random walk

In the CTRW description the probability of just arriving at site s at time t (given the initial condition at site s_0 at time $t_0 = 0$) $R(s, t \mid s_0, 0)$ fulfils the continuous-time recurrence relation

$$R(s, t \mid s_0, 0) = \delta_{s,s_0}\delta(t) + \int_0^t \sum_{s'} \boldsymbol{\eta}(s - s', t - \tau) R(s', \tau \mid s_0, 0)\, \mathrm{d}\tau. \tag{1}$$

The key function, $\hat{\boldsymbol{\eta}}(k, u)$, is the Fourier–Laplace representation of the hopping-waiting-time function $\boldsymbol{\eta}(s - s', t)$; this function completely characterizes the *single-state* CTRW process

$$\hat{\boldsymbol{\eta}}(k, u) = \mathcal{F}_k[\mathcal{L}_u[\boldsymbol{\eta}(s, t)]]. \tag{2}$$

In the continuous space limit (i.e., $x = as$ where $a \to 0$ with $s = 0, \pm 1, \pm 2, \ldots$) the propagator of the continuous-time random walk (CTRW) process reads [18], in the Laplace representation and in one dimension (1D)

$$\hat{\mathbf{G}}(x, u)\, \mathrm{d}x = \frac{\mathrm{d}x}{2\pi} \int_{-\infty}^{+\infty} \hat{\phi}(u)[\mathbf{1} - \hat{\boldsymbol{\eta}}(k, u)]^{-1}\, \mathrm{e}^{-\mathrm{i}kx}\, \mathrm{d}k, \tag{3}$$

where

$$\hat{\phi}(u) = \mathcal{L}_u\left[1 - \int_0^t \eta(k = 0, t')\, \mathrm{d}t'\right] = \frac{1 - \hat{\psi}(u)}{u} \tag{4}$$

is the Laplace representation of the sojourn probability $\phi(t)$ at any site s.

In the particular 'separable' case we get $\hat{\boldsymbol{\eta}}(k, u) = \lambda(k)\hat{\psi}(u)$, then $\lambda(s - s')$ is the hopping-lattice structure of the walks and $\psi(t)$ is the *fundamental* waiting-time density that characterizes the stochastic delay of the walks at any site. In the 1D continuous space limit, assuming a 'finite' one-step variance and a bias to the right we can write

$$\begin{aligned}\lambda(k) &= \mathcal{F}_k[\lambda(s)] = \sum_s \lambda(s)\,\mathrm{e}^{iks} \\ &= p_x\,\mathrm{e}^{\mathrm{i}ka} + (1-p_x)\,\mathrm{e}^{-\mathrm{i}ka} \\ &= 1 + \mathrm{i}\mathcal{V}\tau k - \mathcal{D}\tau k^2 + \mathcal{O}(a^2k^2),\end{aligned} \tag{5}$$

where $\mathcal{V} = (2p_x - 1)a/\tau$ is the external mean velocity (Darcy velocity), $\mathcal{D} = a^2/2\tau$ is the diffusion coefficient in the absence of advection, and τ is a characteristic scale of time[4]. Therefore, in the separable case the Green function is $\hat{\mathbf{G}}(x,u) = \mathcal{F}_k^{-1}[\hat{\phi}(u)[\mathbf{1} - \lambda(k)\hat{\psi}(u)]^{-1}]$. Using approximation (5), integral (3) can analytically be done and the result reads

$$\hat{\mathbf{G}}(x,u) = \frac{\exp\left(-|x|\sqrt{\frac{u}{\hat{\Lambda}(u)\mathcal{D}\tau} + \left(\frac{\mathcal{V}}{2\mathcal{D}}\right)^2} + x\left(\frac{\mathcal{V}}{2\mathcal{D}}\right)\right)}{\hat{\mathbf{\Lambda}}(u)\mathcal{D}\tau\sqrt{\frac{u}{\hat{\Lambda}(u)\mathcal{D}\tau} + \left(\frac{\mathcal{V}}{2\mathcal{D}}\right)^2}}, \tag{6}$$

with

$$\hat{\mathbf{\Lambda}}(u) \equiv \frac{u\hat{\psi}(u)}{1 - \hat{\psi}(u)}. \tag{7}$$

Here $\hat{\mathbf{\Lambda}}(u)$ is the effective transition rate in the corresponding associated generalized (non-Markovian) master equation (ME) that governs the evolution of the Green function of the CTRW process (see [8, 10] and references therein). As we mentioned before (see footnote 4), in the Markovian limit (using an exponential waiting time $\psi(t) = \mathrm{e}^{-t/\tau}/\tau$) the memory kernel is a delta function, so $\mathbf{\Lambda}(t) = \tau^{-1}\delta(t)$, where τ is the characteristic time-scale between each step of the walk.

3. The first passage time distribution in the CTRW approach

Introducing the relation between the FPTD and the propagator in the CTRW approximation, see appendix A, we get

$$\hat{F}(x,u) = \hat{\mathbf{G}}(x,u)/\hat{\mathbf{G}}(x=0,u). \tag{8}$$

Thus we can study the explicit solution for the FPTD in the presence of bias and disorder (to be in $x = L > 0$, having started the walk at $t = 0$ in $x = 0$). The FPTD is given by

$$\hat{F}(L,u) = \exp\left(-\sqrt{\frac{uL^2}{\hat{\mathbf{\Lambda}}(u)\mathcal{D}\tau} + \left(\frac{L\mathcal{V}}{2\mathcal{D}}\right)^2} + \left(\frac{L\mathcal{V}}{2\mathcal{D}}\right)\right), \tag{9}$$

where $\hat{\mathbf{\Lambda}}(u)$ is given in (7). Note that because the bias is to the right, the interesting FPTD is for $x > 0$. The memory kernel $\mathbf{\Lambda}(t)$ can be related to the waiting-time density $\psi(t)$ and the sojourn probability $\phi(t)$ by the integral equation

$$\psi(t) = \int_0^t \mathbf{\Lambda}(t-t')\phi(t')\,\mathrm{d}t'. \tag{10}$$

We are interested in memory kernels which can reproduce typical behaviours in problems of hydrodynamics dispersion [17]. This fact poses some restriction in the models of the waiting-time densities $\psi(t)$ that we will use (for example, the mean current $\mathcal{J}(t) \equiv \mathrm{d}\langle x(t)\rangle/\mathrm{d}t$ should be *well behaved* at all times).

[4] In the Markovian case τ is the parameter that characterizes the Poisson probability of the number of steps in a given interval of time $[0, t]$.

Normal hydrodynamics dispersion is easily reproduced by considering the Markovian case. So using $\hat{\psi}(u) = (1+\tau u)^{-1}$, we get $\hat{\mathbf{\Lambda}}(u) = \tau^{-1}$. In heterogeneous systems, i.e., in the presence of disorder, we should consider non-exponential waiting-time functions $\psi(t)$, which lead to Laplace-dependent kernels $\hat{\mathbf{\Lambda}}(u)$. Note that $\hat{\mathbf{\Lambda}}(u=0)$ is a time integral, which in the context of linear response theory says that the diffusion coefficient is related to the velocity autocorrelation function. If the velocity autocorrelation function ensures the convergence of that integral, the process is normal (diffusive). If the integral diverges we are dealing with a superdiffusive process, and if the integral vanishes we have a subdiffusive process.

3.1. About the Hartree approximation

In general we can say that for a ME in the presence of weak (site) disorder all the inverse moments of the transition probability rate w_s of the ME (from site s) are finite, so we can write for the waiting-time density of the associated CTRW process (i.e., the Hartree approximation [19]) $\hat{\psi}(u) = \sum_{n=0}^{\infty}(-1)^n\left\langle\left(\frac{1}{w_s}\right)^n\right\rangle u^n$. Thus in the asymptotic limit $u \to 0$ we get

$$\hat{\psi}(u \sim 0) \simeq 1 - \tau u, \qquad \text{with} \quad \tau = \left\langle \frac{1}{w_s} \right\rangle.$$

A possible bi-parametric model for a waiting-time density characterizing a weak disordered system is

$$\hat{\psi}(u) = (1+\tau u)^{-b}, \qquad \text{for} \quad \tau > 0, \quad b > 0, \tag{11}$$

thus:

$$\hat{\mathbf{\Lambda}}(u) = \frac{u}{(1+\tau u)^b - 1}. \tag{12}$$

The case when b is an integer is very simple to work out. We just mention that $b = 1$ gives the well-known δ-Dirac kernel, and $b = 2$ gives $\mathbf{\Lambda}(t) = \exp(-2t/\tau)/\tau^2$, etc. For $b > 2$ the kernel $\mathbf{\Lambda}(t)$ goes to zero for $t \to 0$, on the other hand $\mathbf{\Lambda}(t \to \infty) \to 0^+$. Moreover from (12) for the case $b < 2$ we get

$$\mathbf{\Lambda}(t=0) = \lim_{u\to\infty} u\hat{\mathbf{\Lambda}}(u) \to +\infty,$$

and

$$\mathbf{\Lambda}(t=\infty) = \lim_{u\to 0^+} u\hat{\mathbf{\Lambda}}(u) \to 0^+.$$

In figure 1 we show the memory kernel in the time representation, for weak disorder model (11) through a numerical integration of (12) for several b using the LAPIN program [20]. In the case $b = 0.5$ the limit $\mathbf{\Lambda}(t \to 0) \to \infty$ is not plotted due to numerical problems in the integration. Here we emphasize that in this paper we are only interested in the case $b \geqslant 1$, in order to fulfil a well-behaved current (finite at all time) to fit hydrodynamic experiments. It is simple to see by taking the inverse Laplace transform that the waiting time (11) is related to the gamma density to characterize the random delay of the walks [21]:

$$\psi(t) = \frac{1}{\tau}\left(\frac{t}{\tau}\right)^{b-1} \frac{\exp(-t/\tau)}{\Gamma(b)}. \tag{13}$$

We immediately realize that $\psi(t)$ has well-defined moments $\langle t^q \rangle$, $q = 1, 2, 3, \ldots$ (for example, $\langle t \rangle = \tau b$, $\langle t^2 \rangle = (1+b)b\tau^2$, etc). Note that this density becomes sharp in the limit $b\tau^2 \to 0$; in fact, in the limit $b \to \infty, \tau \to 0$ with $\tau b \to$ constant we get the singular result $\psi(t) \to \delta(t - \tau b)$. For values $b < 1$ it is possible to see that the waiting-time density (13) diverges in the limit $t \to 0$, therefore leading to a divergent current at short times. On the

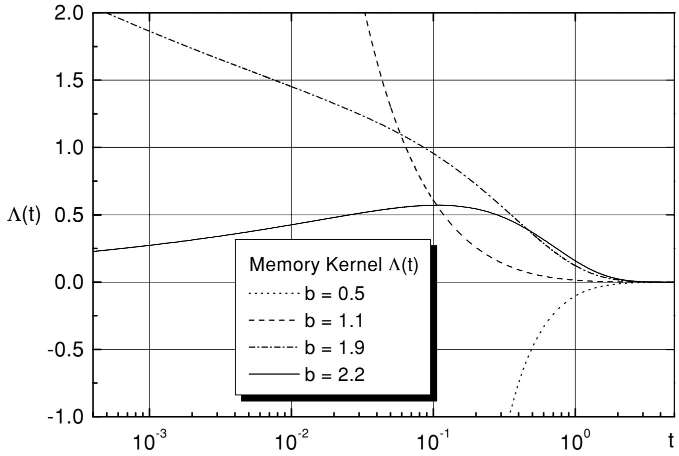

Figure 1. Typical temporal behaviour, in dimensionless time, of the memory kernel $\Lambda(t)$ for weak disorder (11) with $\tau = 1$ and for different values of positive b. Note that for the case $b < 1$ the memory kernel is not always positive.

other hand, for $b > 1$ the renormalized kinetic coefficients turn out to be smaller than in the Markovian case ($b = 1$), as is expected for random walks in the presence of weak disorder. Note that for fixed τ and in the limit $b \to \infty$ the diffusion coefficient asymptotically vanishes because $\hat{\mathbf{\Lambda}}(u = 0) = \int_0^\infty \mathbf{\Lambda}(t)\,\mathrm{d}t = (\tau b)^{-1} \to 0$.

In the presence of strong disorder (subdiffusion problems) some moments of the inverse of the transition rates w_s of the ME may diverge; then in the associated CTRW context the function $\hat{\psi}(u)$ turns to be non-analytic around $u \sim 0$; thus we expect an asymptotic form like (see appendix B)

$$\hat{\psi}(u \sim 0) \sim 1 - C_1 u^\theta, \qquad \text{with} \quad 0 < \theta < 1, \quad C_1 > 0. \tag{14}$$

In this case, for example, we can choose the following bi-parametric model of waiting-time density to characterize a (strong) disordered system

$$\hat{\psi}(u) = \frac{1}{1 + C_1 u^\theta}, \qquad \forall u \text{ with } 0 < \theta < 1. \tag{15}$$

Note that for $\theta < 1$ the constant $C_1 = \tau^\theta$ is not related to any moment of the random delay of the walker because all the integer moments $\langle t^q \rangle$ are divergent quantities. Using model (15) for the waiting-time density, the memory kernel adopts the expression

$$\hat{\mathbf{\Lambda}}(u) = \frac{1}{C_1 u^{\theta-1}} = \frac{u}{(\tau u)^\theta}. \tag{16}$$

In the context of the analysis of a power-law distribution, to characterize random delays free of scaling, we show in the figure of appendix B a plot of a memory kernel associated with the model of strong disorder (14). In particular, in that figure we also show a memory kernel $\mathbf{\Lambda}(t)$ corresponding to a situation of strong disorder but with the possibility of having some finite moments for the random waiting times.

The interesting point, in the statistics of the passage times of the walks, is to analyse the non-trivial competition between the disorder (localization) and the drift (bias). In general for any kind of disorder the expression (9) cannot be transformed back, analytically, into the time representation, but it can be done by numeric integration.

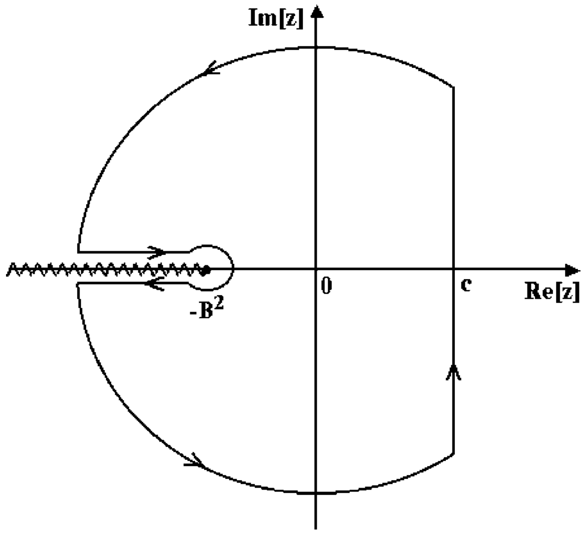

Figure 2. Circuit of the Cauchy integral (17) corresponding to the Markovian case, and for the asymptotic limit in the weak disorder case.

3.2. Markovian case

The Markovian case (the ordered one) can analytically be done and its integration teaches us information which will be useful in the non-Markovian analysis (the disordered one). From (9) and (12) with $b = 1$ we see that we need an inverse Laplace of the form ($F(L, t) \equiv \mathbf{F}(t)$):

$$\begin{aligned}\mathbf{F}(t) &= \frac{1}{2\pi \mathrm{i}} \int_{c-\mathrm{i}\infty}^{c+\mathrm{i}\infty} \exp(-\sqrt{Au + B^2} + B)\, \mathrm{e}^{ut}\, \mathrm{d}u \\ &= \frac{\mathrm{e}^B}{2\pi \mathrm{i}} \oint_{\mathcal{C}} \exp(-\sqrt{z + B^2})\, \mathrm{e}^{zt/A} \frac{\mathrm{d}z}{A},\end{aligned} \tag{17}$$

with

$$B \equiv \frac{L\mathcal{V}}{2\mathcal{D}}, \qquad A \equiv \frac{L^2}{\mathcal{D}}.$$

Here the Cauchy integral $\mathcal{C}$ has to be done in such a way to go on the path $c - \mathrm{i}\infty \to c + \mathrm{i}\infty$, where c is to the right of all the singular points of the integrand. In this case, $\exp(-\sqrt{z + B^2})$ has a branch cut, and thus we can do the Cauchy integral in the form as is shown in figure 2. After some algebra the result is:

$$\mathbf{F}(t) = \sqrt{\frac{A}{4\pi t^3}} \exp\left(B - \frac{B^2 t}{A} - \frac{A}{4t}\right). \tag{18}$$

This result tells us that the presence of a bias, $B \neq 0$, introduces an exponential decay factor $\mathrm{e}^{-B^2 t/A}$ in the FPTD. Physically this means that the peak of the propagator is moving to the right with a finite velocity $\mathrm{d}\langle x(t)\rangle/\mathrm{d}t$. As a matter of fact, this is nothing more than the Laplace shift theorem applied to (17).

Noting from (18) that in the Markovian case, the long-time asymptotic *exponential* contribution can be written in the form

$$\exp\left[\frac{L\mathcal{V}}{2\mathcal{D}}\left(1 - \frac{\mathcal{V}t}{2L}\right)\right], \tag{19}$$

we can identify the term $\mathcal{V}t/2L$ to be proportional to a current, i.e.,

$$\int^{t} \mathcal{J}(t')\,\mathrm{d}t' \sim t\frac{\mathrm{d}\langle x(t)\rangle}{\mathrm{d}t}, \tag{20}$$

a quantity which ultimately is associated with the movement, to the right, of the peak of the propagator.

Our next conjecture is that expression (19) can also be used, asymptotically, in the non-Markovian case when the disorder only introduces a renormalization in the kinetic coefficients. This situation is just what happens in the presence of weak disorder ($b \neq 1$). Thus in order to write the term $\int^{t} \mathcal{J}(t')\,\mathrm{d}t'$ we define the effective velocity:

$$V_{\mathrm{eff}} \equiv \lim_{t\to\infty}\frac{\mathrm{d}}{\mathrm{d}t}\langle x(t)\rangle = \lim_{t\to\infty}\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial}{\partial(\mathrm{i}k)}G(k,t)\bigg|_{k=0}, \tag{21}$$

and write for the non-Markovian case the generalization

$$\exp\left(\frac{L\mathcal{V}}{2\mathcal{D}}\left[1-\frac{1}{2L}\int^{t}\mathcal{J}(t')\,\mathrm{d}t'\right]\right) \simeq \exp\left(\frac{L\mathcal{V}}{2\mathcal{D}}\left[1-\frac{V_{\mathrm{eff}}}{2L}t\right]\right). \tag{22}$$

Therefore if the effective current is not null, the full asymptotic behaviour of the FPTD can be approximated, for any b, by

$$\mathbf{F}(t\to\infty) \sim t^{-3/2}\exp\left(-\frac{L\mathcal{V}}{2\mathcal{D}}\frac{V_{\mathrm{eff}}}{2L}t\right), \tag{23}$$

showing the expected crossover from $t^{-3/2}$ to e^{-Ct}, even in the presence of weak disorder.

3.3. Weak disorder case

From (9) and (12) we see that still in the case of weak disorder it is difficult to analytically calculate the Cauchy integral

$$\mathbf{F}(t) = \frac{\mathrm{e}^{B}}{2\pi\mathrm{i}}\oint_{C}\exp\left(-\sqrt{\frac{zL^{2}}{\hat{\mathbf{\Lambda}}(z)\mathcal{D}\tau}+B^{2}}\right)\mathrm{e}^{zt}\,\mathrm{d}z, \tag{24}$$

with $B \equiv L\mathcal{V}/2\mathcal{D}$. Nevertheless, we know that if the disorder is weak, in general, we obtain asymptotically for $z\to 0$: $zL^{2}/(\hat{\mathbf{\Lambda}}(z)\mathcal{D}\tau) \to z\times\text{const}$. The long-time behaviour of the FPTD can thus be characterized by the approximation (23). From the Green function of the CTRW process it is simple to see that the first moment, in the Laplace representation, is given by:

$$\begin{aligned}\langle\hat{x}(u)\rangle &= \frac{\partial}{\partial(\mathrm{i}k)}\hat{\phi}(u)[\mathbf{1}-\lambda(k)\hat{\psi}(u)]^{-1}\bigg|_{k=0}\\ &= \frac{\mathcal{V}\tau\psi(u)}{u(1-\psi(u))}.\end{aligned} \tag{25}$$

Then when $\hat{\psi}(u)$ is given by (11), noting that $V_{\mathrm{eff}} = \lim_{u\to 0}[u^{2}\langle\hat{x}(u)\rangle]$ and using the Laplace theorem, it follows that $V_{\mathrm{eff}} = \mathcal{V}/b$. Thus for weak disorder the asymptotic behaviour ($t \gg b\tau$) of the FPTD follows using this value of V_{eff} in (23).

As we mentioned, model (11) corresponds to a gamma distribution for the statistics of the random waiting times of the walks. We know that if the statistics is not Poissonian there will be a non-Markovian transient, but because the disorder is weak there is not localization, so at long time there will always be a current restoring the Laplace shift. Thus, as we expected, the crossover to e^{-Ct} appears in the long-time limit of the FPTD. As we commented before, this is a consequence of the asymptotic existence of an effective drift velocity V_{eff}. In figure 3 we have plotted $\mathbf{F}(t)$ given by (9) against approximation (23), for the case $L = 1, \mathcal{V} = 1$ (this

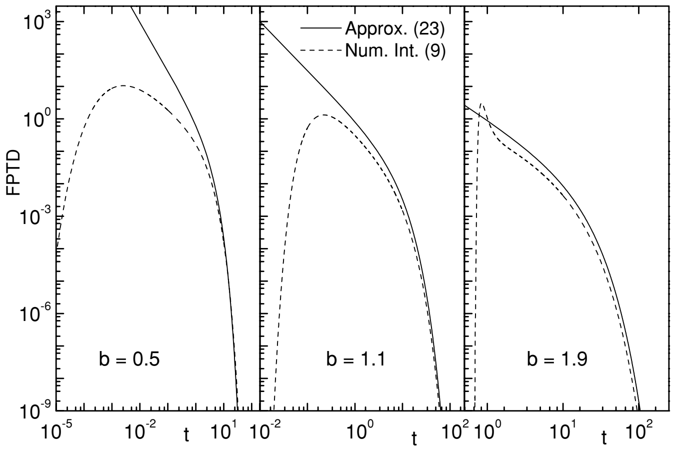

Figure 3. Log–Log plot for the FPTD as a function of t (in dimensionless time) for $L = 1$, $\mathcal{V} = 1$ with $\mathcal{D} = 1$ in the presence of a bias to the right and weak disorder (11). The FPTD is obtained from the Laplace inversion of (9) for $\tau = 1$ and several values of b. The continuous line shows the asymptotic behaviour (23), i.e., the expected crossover from $t^{-3/2}$ to e^{-Ct}.

corresponds to work with dimensionless variables: $x' = x/L$ and $t' = t\mathcal{V}/L$) with $\mathcal{D} = 1$ and different values for the parameter b characterizing weak disorder. From this plot it is simple to check the existence of the aforementioned crossover.

The sharp peak appearing in the transient of the FPTD when $b \gg 1$ can heuristically be understood by analysing the behaviour of the propagator of the CTRW. To see this easily let us calculate the short-time behaviour of the first moment $\langle x(t)\rangle$. Using (25) and (11) it is possible to see that at short times we get

$$\langle x(t \sim 0)\rangle \sim \frac{\mathcal{V}\tau^{1-b}}{\Gamma(1+b)} t^b,$$

in contrast to the long-time behaviour

$$\langle x(t \to \infty)\rangle \sim \frac{\mathcal{V}}{b} t = V_{\text{eff}} t.$$

Thus, even when at long times there is a well-defined effective velocity, at short times when $b > 1$ the peak of the propagator is moving faster than linear in time; this leads to the fact that there are particles that could cross the level $x = L$ (for the first time) earlier than in the Markovian case ($b = 1$). When $b \gg 1$ this effect is enlarged therefore leading to a remarkable peak at short times, see figure 3 for the case $b = 1.9$.

3.4. Strong disorder case

In the presence of strong disorder, for example using the model given by equation (15), it is simple to check that: $zL^2/(\hat{\mathbf{\Lambda}}(z)\mathcal{D}\tau) \sim z^\theta \times$ const., so in principle we should try to solve—at least asymptotically—the following Cauchy integral to get an analytic approximation in the long-time regime

$$\mathbf{F}(t) = \frac{e^B}{2\pi i} \oint_{\mathcal{C}} \exp(-\sqrt{Az^\theta + B^2})\, e^{zt}\, dz, \tag{26}$$

with

$$A = \frac{L^2\tau^{\theta-1}}{\mathcal{D}}, \qquad B \equiv \frac{L\mathcal{V}}{2\mathcal{D}}, \qquad 0 < \theta < 1.$$

Unfortunately this integral is much more complex than that associated with weak disorder; i.e., with $\theta = 1$. For example, the branch cut associated with the weak disorder case (see figure 2) does not arise trivially from (26), in the limit $\theta \to 1$.

In the strong-disorder case, using (25) and (14), the asymptotic moment gives $\langle \hat{x}(u \sim 0)\rangle \sim \mathcal{V}\tau^2(\tau u)^{-(\theta+1)}$, then using the Tauberian theorem [10] we find that the asymptotic current behaves like

$$\mathcal{J}(t \to \infty) \propto \lim_{t\to\infty} \frac{\mathrm{d}}{\mathrm{d}t}\langle x(t)\rangle \sim \lim_{t\to\infty} t^{\theta-1}, \quad \theta \in (0, 1). \tag{27}$$

This means that the current eventually will be null, even in the presence of *no absorbing boundary condition*! This is a remarkable result that was, in fact, pointed out in the pioneering works of the CTRW (see references [8, 10] and references therein).

Noting that in (26) we can introduce a series expansion for $\exp(-\sqrt{Az^\theta + B^2} + B)$ to carry out a perturbation in $z^\theta \sim 0$ (if $A/B^2 \ll 1$), we get (when $B \neq 0$ and $\theta \neq 1$)

$$\begin{aligned}\exp(-\sqrt{Az^\theta + B^2} + B) \approx 1 &- \frac{A}{2B}z^\theta + \frac{A^2(1+B)}{8B^3}z^{2\theta} - \frac{A^3(3+3B+B^2)}{48B^5}z^{3\theta} \\ &+ \frac{A^4(15B^2+B^4+3B(5+2B^2))}{384B^8}z^{4\theta}\cdots.\end{aligned} \tag{28}$$

Then the asymptotic behaviour of $\mathbf{F}(t)$ follows from the application of the Tauberian theorem to each of these contributions. Assuming α to be irrational, we know that asymptotically for $u \to 0$ $(t \to \infty)$

$$\mathcal{L}_u^{-1}[u^{(n+1)\alpha-1}] \sim \frac{t^{-(n+1)\alpha}}{\Gamma(1-(n+1)\alpha)}, \tag{29}$$

with

$$0 < \alpha < 1, \quad n = 0, 1, 2, \ldots,$$

where $\Gamma(x)$ is the gamma function [21]. Therefore, in particular, from (28) and (29) when θ is irrational we obtain the alternating converging series [19][5]

$$\begin{aligned}\mathbf{F}(t) \approx -\frac{A}{2B}\frac{t^{-(\theta+1)}}{\Gamma(-\theta)} &+ \frac{A^2(1+B)}{8B^3}\frac{t^{-(2\theta+1)}}{\Gamma(-2\theta)} - \frac{A^3(3+3B+B^2)}{48B^5}\frac{t^{-(3\theta+1)}}{\Gamma(-3\theta)} \\ &+ \frac{A^4(15B^2+B^4+3B(5+2B^2))}{384B^8}\frac{t^{-(4\theta+1)}}{\Gamma(-4\theta)}\cdots.\end{aligned} \tag{30}$$

When θ is rational, the change in this result is that terms in which $n\theta$ is an integer ought to be omitted from the sum. Note that result (30) does not apply in the limit $\theta \to 1$. In figure 4 we have plotted $\mathbf{F}(t)$ from (9) using (16) for the case $\theta = 1/2$, against the *dominant* long-time limit:

$$\mathbf{F}(t) \sim t^{-(1+\theta)}. \tag{31}$$

From this plot we see that the transient and the long-time regime of the FPTD is mainly controlled by the asymptotic power law (31). So in the presence of strong disorder there is not a crossover to e^{-Ct} as occurs with weak disorder ($\theta = 1$). The strong disorder breaks the application of the Laplace shift theorem.

[5] In fact, this expansion is equivalent to the asymptotic behaviour of the FPTD presented by Scher and Montroll [19]. See appendix A to be aware of the approximation made in calculating the FPTD for non-Markovian walks.

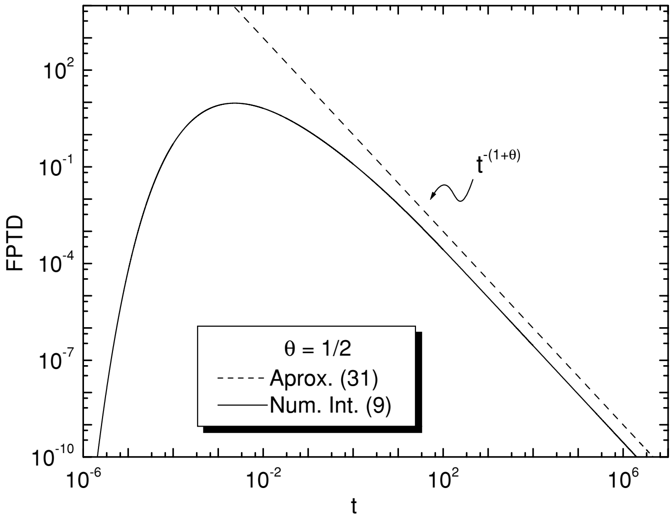

Figure 4. Log–Log plot for the FPTD as a function of t (in dimensionless time) for $L = 1$, $\mathcal{V} = 1$ with $\mathcal{D} = 1$ in the presence of a bias to the right and strong disorder (15). The FPTD is obtained from the Laplace inversion of (9) for $\tau = 1$ and $\theta = 0.5$ against the asymptotic power-law behaviour (31).

4. Transport with multiple families of paths

In this section, we are going to use the previous formulation in calculating the passage time statistics of asymmetric walks, but in the particular case when there are multiple families of paths [22]. This is an important step in order to address problems of hydrodynamics dispersion considering the possibility that the transport could be affected by stagnant domains, etc (i.e., connected and non-interconnected pores). In other words, it is well known that most natural porous media, such as oil reservoirs, contain some dead-end pores. A fluid in such pores communicates with the flowing fluids only by molecular diffusion. Such a mechanism of mass transfer between the flowing fluids and the dead-end pores was invoked many years ago [23, 24]. In particular in a very interesting paper concerning *non-interconnected pores* (porosity and permeability), Bouchaud *et al* [25] studied stagnation effects in hydrodynamics dispersion. Here we are going to implement that model in our approach, in order to consider also molecular diffusion in the description.

One of us in a previous paper [17] has shown that transport in the presence of multiple paths can be understood in the context of the multistate CTRW approach [26]. Thus instead of the continuous-time recurrence relation (1) we now use

$$R_l(s, t \mid s_0, 0) = \delta_{s,s_0}\delta_{l,l_0}\delta(t) + \int_0^t \sum_{l'} \sum_{s'} \eta_{ll'}(s - s', t - \tau) R_{l'}(s', \tau \mid s_0, 0)\, \mathrm{d}\tau. \tag{32}$$

The matrix Green function, i.e., the solution of the multistate CTRW process, is analogous to the one we have already mentioned in (3), but now considering matrices in order to take into account the internal states of the multistate CTRW process, see [17].

It is possible to see that a generalization of the Bouchaud *et al* model can be implemented by using the following waiting-time matrix:

$$\eta(k, t) = \begin{pmatrix} \lambda(k)\psi_1^T(t)\phi_1^E(t) & \psi_{12}^E(t) \\ \phi_1^T(t)\psi_{21}^E(t) & 0 \end{pmatrix}, \tag{33}$$

where

$$\phi_1^T(t) = 1 - \int_0^t \psi_1^T(t')\,\mathrm{d}t' \tag{34}$$

is the sojourn probability *into* the transport path (labelled by state $l = 1$), and $\psi_{12}^E(t)$, $\psi_{21}^E(t)$ are the waiting-time densities associated with the exchange of the paths. Consistently

$$\phi_l^E(t) = 1 - \int_0^t \psi_{l'l}^E(t')\,\mathrm{d}t', \qquad \{l, l'\} = 1, 2 \tag{35}$$

are the sojourn probabilities from the exchange mechanism.

A *dynamical* disorder model related to that of [25] can be considered by using

$$\psi_{12}^E(t) = \psi(t) \tag{36}$$

which is the waiting-time density *from* the stagnant domains (labelled by state $l = 2$) to the transport path, and

$$\psi_{21}^E(t) = \nu_{21}\exp[-\nu_{21}t], \tag{37}$$

characterizing the reverse process, i.e., the probability density to jump to the stagnant domains *from* the transport path, thus $\phi_1^E(t) = \exp[-\nu_{21}t]$. On the other hand, if the hopping mechanism *into* the transport path is Markovian, we can use

$$\psi_1^T(t) = \frac{1}{\tau}\exp\left[-\frac{t}{\tau}\right]. \tag{38}$$

From definitions (36), (37) and (38), after some algebra and taking the Laplace transform we get from (33) that

$$\hat{\eta}(k, u) = \begin{pmatrix} \lambda(k)(u + \tau^{-1} + \nu_{21})^{-1}/\tau & \hat{\psi}(u) \\ \nu_{21}(u + \tau^{-1} + \nu_{21})^{-1} & 0 \end{pmatrix}. \tag{39}$$

It is simple to see that if $\lambda(k)$ characterizes a directed random walk in a 1D regular lattice of spacing a, we have to use $\lambda(k) = \mathrm{e}^{\mathrm{i}ka}$; we will come back to this case in section 4.2. In addition, in order to compare our model with the quench disorder directed random walk model of [25] we should identify $a/\tau = V$, $\nu_{21} = p/\tau$, and the distribution of the random waiting times *from* the stagnant domain (36) should be characterized by

$$\hat{\psi}(u) = \int_0^\infty \mathrm{e}^{-ut}\psi(t)\,\mathrm{d}t = \sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\langle t^n\rangle u^n. \tag{40}$$

In figure 5 we show a sketch of a directed random walk with quench disorder (Bouchaud and Georges model), and the present molecular diffusion model with random stagnant domains (dynamical disorder model). The case when the random waiting times *from* the stagnant domain are free of scaling can also be worked out in a similar way [17].

Now, let us introduce in (39) a 1D (continuous in space) model with molecular diffusion, thus we can consider the lattice *hopping* structure $\lambda(k)$ to be approximated as in (5) by

$$\begin{aligned}\lambda(k) &= p_x\,\mathrm{e}^{\mathrm{i}ka} + (1 - p_x)\,\mathrm{e}^{-\mathrm{i}ka} \\ &= 1 + \mathrm{i}(2p_x - 1)ak - \tfrac{1}{2}a^2k^2 + \mathcal{O}(a^2k^2).\end{aligned}$$

Using the initial condition that the walker was in $x = 0$ at $t = 0$ into the transport path ($l = 1$), the Green function (see [17]) reads:

$$\hat{\mathbf{G}}(k, u) = \frac{2\tau}{a^2k^2 - \mathrm{i}2ak(2p_x - 1) + 2\tau[\nu_{21}(1 - \hat{\psi}(u)) + u]}, \tag{41}$$

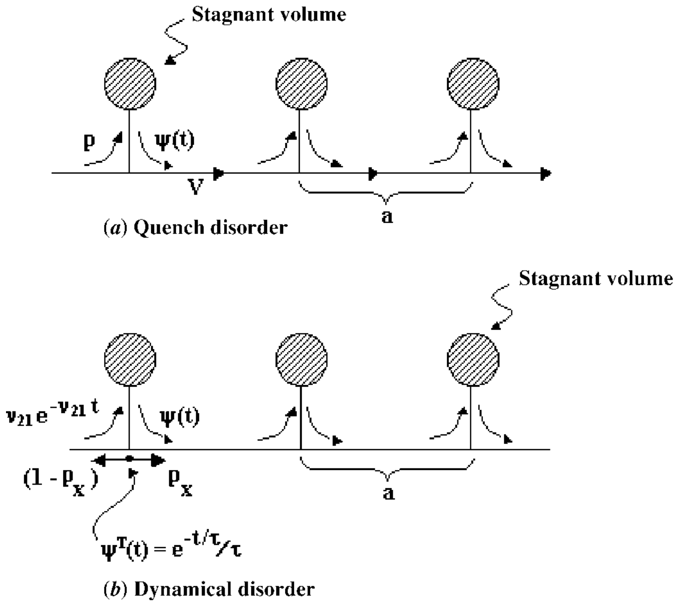

Figure 5. (*a*) Sketch of a directed random walk in the presence of stagnant domains, using a quench disorder modelling. (*b*) Sketch of a random walk in the presence of stagnant domains, using a dynamical disorder modelling.

and so the FPTD (in the Laplace representation) to cross the level $x = L$ is

$$\hat{F}(L,u) = \exp\left(-\sqrt{\frac{L^2\tau[\nu_{21}(1-\hat{\psi}(u))+u]}{a^2/2} + \left(\frac{L(2p_x-1)}{a}\right)^2} + \left(\frac{L(2p_x-1)}{a}\right)\right)$$
$$= \exp\left(-\sqrt{\frac{uL^2}{\hat{\Lambda}_{\mathrm{MP}}(u)\mathcal{D}\tau} + \left(\frac{L\mathcal{V}}{2\mathcal{D}}\right)^2} + \left(\frac{L\mathcal{V}}{2\mathcal{D}}\right)\right), \tag{42}$$

where in the second line we have used the same notation as in (9). Thus we see that for the *multiple paths* model (with disorder) we can define an effective *memory kernel*

$$\hat{\Lambda}_{\mathrm{MP}}(u) = \frac{u}{\tau[\nu_{21}(1-\hat{\psi}(u))+u]}. \tag{43}$$

Therefore using the multiple paths model (39), we see that asymptotically at long times the dominant behaviour of the FPTD is controlled by the competition between $(1-\hat{\psi}(u))$ against u; thus when there is simultaneously a bias and disorder the occurrence of the crossover $t^{-3/2}$ to e^{-Ct} will have the same analysis as we have studied before (without multiple paths, see equation (23)). Nevertheless, the inclusion of multiple paths changes the description of the *transient* of the FPTD, therefore introducing finite-size effects. That result is crucial in the context of oil-recovery experiments in porous rocks. We remark that for the present model of multiple paths, a possible anomalous long-time behaviour of the FPTD is controlled by the waiting time *into* the stagnant domains. Moreover, the occurrence of an asymptotic dominant behaviour $\sim\mathrm{e}^{-Ct}$, for the FPTD decay, appears if the waiting-time density *into* the stagnant domains has finite moments. In other words, only a waiting time as in (40) will lead to a non-null effective velocity V_{eff} (see (20) and (44)).

It is interesting to compare the *effective* memory kernel (43) with the one that appears without multiple paths $\hat{\mathbf{\Lambda}}(u) = u\hat{\psi}(u)/(1-\hat{\psi}(u))$. Here we should emphasize that in the last case $\hat{\psi}(u)$ is the waiting time of a *single-state* random walk (see equation (7)). Nevertheless, in (43) $\hat{\psi}(u)$ is the waiting time of a *two-state* random walk when the walker is into the stagnant domains. Note that the waiting time of the walker *into* the transport paths has been taken to be exponential (see (38)). It is simple to see from equation (43) that the present multiple paths model reduces to the so-called Coats–Smith profile when $\psi(t) = \psi_{21}^{E}(t)$ and $\nu_{21} \equiv K_c$ (see [17]).

From the previous results we can conclude some expressions for the kinetic coefficients. In general, for the present *two-state* random walks model with arbitrary $\hat{\psi}(u)$ we get

$$\begin{aligned}\langle\hat{x}(u)\rangle &= \frac{a(2p_x-1)}{\tau(u+\nu_{21}(1-\hat{\psi}(u)))^2}\\ &= \frac{\mathcal{V}}{(u+\nu_{21}(1-\hat{\psi}(u)))^2},\end{aligned} \tag{44}$$

where in the last expression we have used our old notation (see equation (5)). Note that in the particular case when $\psi(t)$ has a long-time tail (characterized by $\hat{\psi}(u) \sim 1-(\tau u)^{\theta}$) the current of particles is asymptotically at long times given by $\mathcal{J}(t) \propto \mathcal{V}/(\nu_{21}\tau)^2(t/\tau)^{2(\theta-1)}$. Therefore announcing a faster power-law decay in comparison with the one from a *single-state* anomalous random walks model, see (27). From our *two-state* random walks model, with arbitrary $\hat{\psi}(u)$, we get for the second moment

$$\langle\hat{x}(u)^2\rangle = \frac{2\mathcal{V}^2}{(u+\nu_{21}(1-\hat{\psi}(u)))^3} + \frac{2\mathcal{D}}{(u+\nu_{21}(1-\hat{\psi}(u)))^2}. \tag{45}$$

Note that *only* in the case of null transition towards the stagnant domains ($\nu_{21} = 0$), the dispersion is normal, i.e., $\{\langle x(t)^2\rangle - \langle x(t)\rangle^2\} = 2\mathcal{D}t$. In the particular case when the waiting-time density (from the stagnant domains) can be expressed as in (40), the dispersion coefficient of the process turns out to be time-dependent

$$\begin{aligned}D &= \lim_{t\to\infty}\{\langle x(t)^2\rangle - \langle x(t)\rangle^2\}/2t\\ &\cong \frac{\mathcal{D}}{\mathcal{V}^2}U^2 + \frac{\langle t\rangle}{2\mathcal{V}^2}U^4\nu_{21}t.\end{aligned} \tag{46}$$

Only in the limit $\nu_{21}t \ll 1$ we get a constant behaviour $D \propto U^2$, where U is the macroscopic mean velocity of the test particle. This means that the fluctuation in the transient time, induced by the delay in the stagnant domains, gives rise to an enhanced diffusion phenomenon. Thus, as a result of this multiple paths model, the hydrodynamics dispersion coefficient of the process is expected to be enhanced linearly in time. As we commented before, $\mathcal{D}$ is the diffusion coefficient in the absence of advection and $\mathcal{V}$ is the Darcy velocity. On the other hand, $\langle t\rangle$ is the mean *trapped* time into the stagnant domains and ν_{21} is proportional to the fraction of dead-end volumes in the heterogeneous porous media. Note that in expression (46) we have used the definition of the *mean* velocity U as

$$U = L/\mathcal{T} = \frac{\mathcal{V}}{\nu_{21}\langle t\rangle + 1},$$

where $\mathcal{T} = \int_0^\infty t'F(L,t')\,\mathrm{d}t' = -\partial\hat{F}(L,u)/\partial u|_{u=0}$ is the mean value of the time that the test particle need to cross the level L for the first time, i.e., the mean first passage time. A more accurate value for the macroscopic *mean* velocity would be $\langle L/t'\rangle$. Unfortunately the quantity $\langle 1/t'\rangle$ is hard to calculate analytically, but it can be done numerically from $F(L,t')$.

In general, our formula for the FPTD gives us the possibility of studying the transient of test particles, as is needed in the analysis of oil recovery experiments in heterogeneous

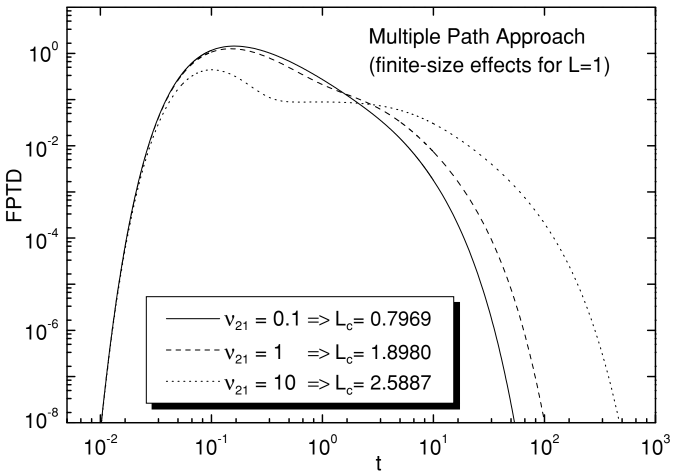

Figure 6. Log–Log plot for the FPTD as a function of t (in dimensionless time) for $L = 1$, $\mathcal{V} = 1$ with $\mathcal{D} = 1$ in the presence of a bias to the right and weak disorder (11) in the multiple paths approach. The FPTD is obtained from the Laplace inversion of (42) for $\tau = 1$ and $b = 1.1$ for several values of ν_{21}, the inset shows the corresponding critical length.

media. In addition, we mention here that from our approach we can go beyond the so-called Coats–Smith profile [24, 17] because we can introduce disorder in the transport description. In figure 6 we show the FPTD from (42) for the case $L = \mathcal{V} = \mathcal{D} = \tau = 1$, using for $\hat{\psi}(u)$ the model of weak disorder (11) with $b = 1.1$, and for several values of the fraction of non-interconnected pores ν_{21}. From this figure it is possible to realize the important difference in the transient regime of the FPTD when it is compared with the same weak disorder model $\psi(t)$ but without multiple paths. In other words, the multiple paths approach incorporates the notion of a fraction of non-interconnected pores and in addition the distribution of porous sizes through the waiting-time model (40). The multiple paths model leads to finite-size effects as was reported in a previous work [17]. We remark that in the present paper we are also considering the inclusion of weak disorder in the characterization of the critical length. The case $\nu_{21} = 0$ corresponds to the *single-state* Markovian random walks.

4.1. About the finite-size effects

From (43) it is possible to characterize a critical length L_c from which we can analyse finite-size effects in this non-Markovian multiple path model of disorder. In order to define a characteristic length we now introduce the dimensionless variables

$$x' = x/L, \qquad t' = t\mathcal{V}/L.$$

If we had a Gaussian profile the maximum of the FPTD $F_{\mathrm{Gauss}}(t, x)$ would be located at the dimensionless time [17]:

$$t'_{\mathrm{Max}} = -\frac{3}{B} + \sqrt{\left(\frac{3}{B}\right)^2 + (2x')^2}, \qquad B \equiv \frac{L\mathcal{V}}{2\mathcal{D}}.$$

In the case when $\hat{\psi}(u)$ is given by (40) (i.e., characterizing a heterogeneous medium) it is possible to see, from (43), that a Gaussian behaviour is approached when

$$\varkappa_c \equiv \frac{(\nu_{21}\langle t\rangle + 1)}{\nu_{21}\langle t^2\rangle} \gg u,$$

where $\varkappa_c^{-1}$ is a characteristic non-Markovian time-scale. Then, finite-size effects are expected to occur if the condition $t'_{\mathrm{Max}} \lesssim \varkappa_c^{-1}\mathcal{V}/L$ is fulfilled. Going back to the old variables we get that the condition to find finite-size effects is

$$x \lesssim \frac{3\mathcal{D}}{\mathcal{V}}\sqrt{\left(\frac{\nu_{21}\langle t^2\rangle \mathcal{V}^2/\mathcal{D}}{6(\nu_{21}\langle t\rangle + 1)} + 1\right)^2 - 1} \equiv L_c, \tag{47}$$

i.e., if $x \gg L_c$ we do not expect finite-size effects. Note that for $\nu_{21} \to 0$ the finite-size effects are not expected. In particular, using the weak disorder model (11) to characterize the random waiting times from the stagnant domains we get the critical length

$$L_c = \frac{3\mathcal{D}}{\mathcal{V}}\sqrt{\left(\frac{\nu_{21}(1+b)b\tau^2}{6(\nu_{21}\tau b + 1)}\frac{\mathcal{V}^2}{\mathcal{D}} + 1\right)^2 - 1}.$$

As we commented before, in figure 6 we have plotted the FPTD for the case $L = 1$ and weak disorder (11) for several values of ν_{21}, thus from this plot we can test our finite-size characterization. For example, for the values of non-interconnected pore fraction ν_{21} $(= 0.1, 1, 10)$ we get for the critical length L_c $(= 0.7969, 1.8980, 2.5887)$, thus showing that by increasing ν_{21} the finite-size effects are enlarged. From this plot it is simple to see the remarkable 'bump' occurring at early times for the case $\nu_{21} = 10$, this is so because $L \lesssim L_c$. If we had plotted the same FPTD but for $L \gg L_c$ (for example 5, 10, etc) this particular anomalous transient would have disappeared; in contrast, for L $(= 0.5, 0.1)$ using the same value of ν_{21} the finite-size effects are enlarged. Another very interesting parameter to test this finite-size condition is the value of the Darcy velocity $\mathcal{V}$. On the other hand, note that the dependence of L_c with a large diffusion coefficient $\mathcal{D}$ can heuristically be understood in terms of pure diffusion. Other models of weak disorder can also be analysed in a similar way; for example, as is expected, by increasing the dispersion of the random waiting times from the stagnant domains, $\propto\langle t^2\rangle$, the finite-size effects are enhanced. Here it is interesting to point out that by introducing $\psi(t) = \psi_{21}(t)$, i.e., using $\langle t^2\rangle = 2\nu_{21}^{-2}$, and $\langle t\rangle = \nu_{21}^{-1}$ in (47) the critical length of the Coats–Smith profile is reobtained. So our result (47) generalizes the finite-size analysis of [17] for the case when there is disorder in the medium. We emphasize that in [17] the analysis of L_c was done in a homogeneous approximation (also the scaling x', t' was different), i.e., using the Coats–Smith equation. Interestingly, from the present results, the long transient and the plateau of the finite-size effect could lead to the misleading interpretation that the decay of the FPTD is a power law. But we emphasize—as we have already proved—that in the presence of weak disorder, at very long time after the crossover, the FPTD decay is controlled by a drift contribution $\propto e^{-Ct}$ (see our remark after equation (43)).

4.2. About the directed random walk model

In the directed random walk case, i.e., when $\lambda(k) = e^{ika}$, it is not necessary to go to the continuous limit ($ka \to 0$) to do all the calculations. In fact it is possible to see that the analytical expression for the FPTD (in the Laplace representation) is

$$\begin{aligned}\hat{F}(L,u) &= \hat{G}(L,u)/\hat{G}(0,u)\\ &= (1 + \tau[u + \nu_{21}(1 - \hat{\psi}(u))])^{-L/a}.\end{aligned} \tag{48}$$

Here, it is important to compare this expression with the one coming from the *quenched disorder* model of [25]

$$\hat{F}_{\mathrm{QD}}(L,u) = e^{-Lu/V}(1 - p + p\hat{\psi}(u))^{L/a}. \tag{49}$$

Note for example that for the particular case $p \to 0$, this solution gives $\hat{F}_{\rm QD}(L, u) = {\rm e}^{-Lu/V}$, which corresponds to the sharp distribution: $F_{\rm QD}(L, t) \to \delta(t - L/V)$. A solution that is conceptually different from the one that is obtained using (48) in the corresponding particular limit $\nu_{21} \to 0$, i.e., the Poisson solution $F(L, t) \to t^{L/a-1}\,{\rm e}^{-t/\tau}/\{\tau(L/a - 1)!\}$.

Here we would like to point out that from equation (49) and in the limit $p \to 1$ the solution gives [25]

$$F_{\rm QD}(L, t)|_{p=1} = \begin{cases} \mathcal{L}_u^{-1}[\hat{\psi}(u)^{L/a}]|_{t-L/V} & \text{for } t > L/V \\ 0, & \text{for } t < L/V. \end{cases}$$

Nevertheless, from our model, using (39) in the case when there is no hopping at all (i.e., $\lambda(k) = 1$) this spurious result does not appear.

5. Discussion

From the present work we can understand the transient and the long-time behaviour of the statistics of passage times of asymmetric non-Markovian walks. We have discussed the first passage time distribution in the presence of bias and disorder, in the context of the continuous-time random walk theory. A detailed and comprehensive analysis in terms of the important parameters of the problem has been done; in particular, we have shown the temporal behaviour of the associated memory kernel $\Lambda(t)$ (the velocity autocorrelation function of the process) for different classes of disorder.

The results that we have presented are important in the analysis of hydrodynamics dispersion of stratified disordered media [27–29]. As a matter of fact, if in addition there are many transport paths—which could appear due to stagnant domains in the heterogeneous porous media—the situation has been analysed considering internal states in the master equation, to emulate the different families of paths that may appear in the random media [22]. In the present paper we focus the problem of the presence of stagnant volumes, but our approach can also be extended to consider fractures in the porous media as alternative paths [17].

We have analysed the occurrence of the crossover $t^{-3/2}$ to ${\rm e}^{-Ct}$ in the first passage times distribution when there is bias and weak disorder in the transport process. We have compared the statistics of these passage times, with and without multiple paths, and we have shown the relevance of the multiple paths approach to understand the problem of the transient anomalous dispersion (finite-size effects). With all of this information we have calculated some kinetics coefficients; in particular, we have shown the occurrence of an enhanced dispersion in the presence of stagnant domains (see (46)). In addition, all the transient information is encoded in formula (42), and any moment of the passage times can easily be calculated by differentiation of $\hat{F}(L, u)$. In the case of weak disorder the finite-size analysis has been carried out generalizing our previous studies on the Coats–Smith profile [17], in particular the critical length L_c has been given in terms of the parameters that characterize the weak disorder (see equation (47)). A comparison with the model of directed random walks with quenched disorder [25] has been quoted in section 4.2.

To summarize, the first passage time distribution of a test particle in a heterogeneous medium has been estimated in the context of the Hartree approximation (CTRW modelling). Therefore, the response to the injection of a pulse when there are stagnant domains and when the transport is controlled by molecular diffusion and advection has been presented. Our approach allows us to calculate not only the long-time behaviour but also the transient of complex transport processes, like the anomalous hydrodynamics dispersion we have reported in this paper. As a matter of fact, in the petroleum industry, inter-well tracer tests are one of the most important tools for the diagnostic and characterization of the oil reservoir in the secondary oil recovery process [30]. An adequate interpretation of the residence time of the tracer into the well gives essential information about the disordered matrix of the porous media [31]. In a future work, we will analyse these experiments in heterogeneous porous rocks by doing nonlinear least-squares fits from our analytic solution in the Laplace representation.

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Appendix A. Concerning the first passage time distribution

Here we are going to present an alternative point of view to understand the meaning of the convolution equation (8) governing the FPTD [8]. From this approach it will be clear that the definition of the FPTD used in the context of the CTRW is *only exact* for the Markovian case, or alternatively under the assumption of the *synchronized condition*. It is interesting to remark that, to our knowledge, the only references wherein this fact has been considered are [8, 16, 17, 32].

Let the conditional probability $\Pr(\mathcal{A} \mid \mathcal{C})$ for the event $\mathcal{A}$, given that the event $\mathcal{C}$ is sure, be written in the form

$$\Pr(\mathcal{A} \mid \mathcal{C}) = \sum_{\{\mathcal{B}_n\}} \Pr(\mathcal{A} \cap \mathcal{B}_n \mid \mathcal{C}), \qquad \mathcal{A} \cap \mathcal{B}_n \neq \emptyset, \quad \forall n, \tag{A.1}$$

where $\{\mathcal{B}_n\}$ is a set of ordered events. Consider now the particular situation when

$$\begin{aligned} \mathcal{A} \quad &\Rightarrow \quad \text{event } x(t) \\ \mathcal{B}_n \quad &\Rightarrow \quad \text{event } x(t_n) = x^* \text{ for the first time} \\ \mathcal{C} \quad &\Rightarrow \quad \text{event } x(t_0) = x_0. \end{aligned}$$

Then, (A.1) can be written in the form

$$P(x, t \mid x_0, t_0) = \sum_{\{n\}} P(x, t \mid x^*, t_n; x_0, t_0) F(x^*, t_n \mid x_0, t_0), \quad t \neq t_0, \tag{A.2}$$

where $F(x^*, t_n \mid x_0, t_0)$ is the probability distribution to cross the level x^* at time t_n for the first time, having started the walk from x_0 at time t_0. If we now assume that the time is continuous, we can write

$$P(x, t \mid x_0, t_0) = \phi(t - t_0)\delta_{x,x_0} + \int_{t_0}^{t} \mathrm{d}t'\, P(x, t \mid x^*, t'; x_0, t_0) F(x^*, t' \mid x_0, t_0), \tag{A.3}$$

where $\phi(t - t_0)$ is the sojourn probability to remain in x_0 without having left this site since the beginning of the walks. In particular we can use (A.3) for $x(t) = x^*$ and $t_0 = 0$, then we get

$$P(x^*, t \mid x_0, 0) = \phi(t)\delta_{x^*,x_0} + \int_{0}^{t} \mathrm{d}t'\, P(x^*, t \mid x^*, t'; x_0, 0) F(x^*, t' \mid x_0, 0). \tag{A.4}$$

A schematic draw representing some of the paths contributing to the continuous-time relation (A.4) is shown in figure 7. If the stochastic process is Markovian we know that $P(x_j, t_j \mid x_{j-1}, t_{j-1}; \cdots; x_0, t_0) = P(x_j, t_j \mid x_{j-1}, t_{j-1})$, then we can write from (A.4) the relation

$$P(x^*, t \mid x_0, 0) = \phi(t)\delta_{x^*,x_0} + \int_{0}^{t} \mathrm{d}t'\, P(x^*, t \mid x^*, t') F(x^*, t' \mid x_0, 0). \tag{A.5}$$

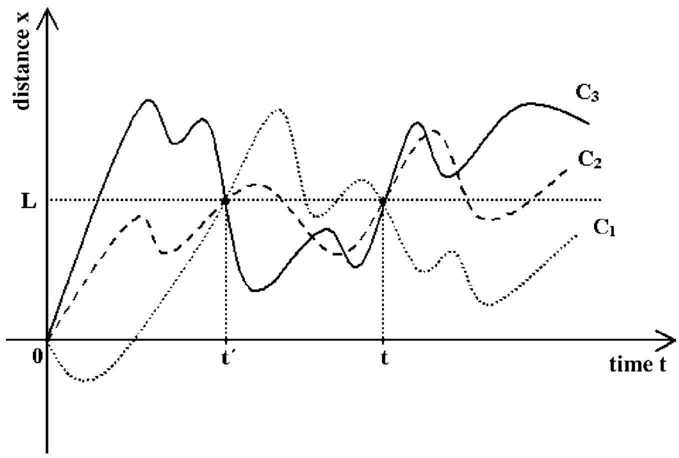

Figure 7. Schematic drawing representing some realizations (in dimensionless distance and time) contributing to the definition of the FPTD. Note that the realization C_3 does not contribute in the definition (A.4), but it does in the construction of a Markov propagator $P(x^*, t \mid x^*, t')$.

Therefore, assuming that the space and the time are homogeneous we get

$$P(x^*, t \mid x_0, 0) = \phi(t)\delta_{x^*,x_0} + \int_0^t \mathrm{d}t'\, P(0, t - t' \mid 0, 0)F(x^*, t' \mid x_0, 0). \qquad \text{(A.6)}$$

Thus the probability distribution to cross the level L at time t for *the first time*, having started the walk from x_0 at time $t_0 = 0$, can be solved by a Laplace transform of the convolution equation (A.6), i.e.,

$$\hat{F}(L, u \mid x_0, 0) = \frac{\hat{P}(L, u \mid x_0, 0)}{\hat{P}(0, u \mid 0, 0)}, \qquad \text{with} \quad L \neq x_0. \qquad \text{(A.7)}$$

This result is exact for any Markovian process.

The specific assumption generally made in defining the CTRW model is that the intervals between successive steps of the process, $\tau_n = t_n - t_{n-1}$, are identically distributed independent random variables characterized by the distributions

$$\psi_{(n)}(\tau) = \int_0^\tau \psi_{(n-1)}(t)\psi(\tau - t)\,\mathrm{d}t, \quad n = 1, 2, 3, \ldots.$$

Let us emphasize that the single-state CTRW is, in general, a non-Markovian process, since at any time one has to know both the position of the walker and the time at which the last step was made in order to predict the further course of the random walk, except for the exponential form of the *fundamental* waiting-time density $\psi(t)$ [10]. Here, it is important to remark that, due to the particular convolution structure of the CTRW propagator, it is possible to conclude that the FPTD is related to a synchronized conditional probability by an extension of the renewal equation for an arbitrary waiting-time density $\psi(t)$ [32]:

$$P(x^*, t \mid x_0, 0) = \phi_{(0)}(t)\delta_{x^*,x_0} + \int_0^t \mathrm{d}t'\, \mathcal{P}^S(x^*, t \mid x^*, t')F(x^*, t' \mid x_0, 0), \qquad \text{(A.8)}$$

where $\mathcal{P}^S(x, t \mid x', t')$ is now the synchronized conditional probability and $\phi_{(0)}(t)$ is the sojourn probability for the first jump [8]. Under the *synchronized condition* there are two possible choices for the *special* waiting-time density $\psi_{(0)}(t)$. First, we may consider the transition at $t = 0$ as the first one [33]. Second, we may consider Feller's stationary ensemble case $\psi_{(0)}(t) = \psi(t)$ [8, 34]. Then as a result of the synchronized condition, in both cases the FPTD is given by (A.7). Taking $x_0 = 0$ the solution (A.7) is the result we used in (8). In the multistate CTRW case the present discussion is slightly more complex because the synchronization condition must also be extended to the configuration of the internal states, but the main idea is the same (see appendix B of [17] and references therein).

To end this discussion, let us mention that (A.7) is just the formula used in the work of Scher and Montroll [19]. Also a related exact formula was presented in a pioneering work by Montroll when he studied a *Markovian chain* [35]. There, the quantity $F(l_1 - l_0, z) = G(l_1 - l_0, z)/G(0, z)$ was the generating function of all walks which start at l_0 and reach l_1 for *the first time* at the nth step ($n = 1, 2, \ldots, \infty$), while $G(l_1 - l_0, z)$ was the generating function which corresponds to the sum over all paths which start at l_0 and end at l_1. It is interesting to point out that a rigorous perturbation approach, in terms of Terwiel's cumulants, was presented in [14] to calculate the FPTD in random media (without bias). In the presence of disorder and a small bias the mentioned perturbation theory can also be considered as was presented in [36].

Appendix B. On the Abel probability distributions

Abel was probably the first to give an application of fractional calculus [37]. He used derivatives of arbitrary order to solve the isochrone problem in classical mechanics, and the integral equation he worked out was precisely the one Riemann used to define fractional derivatives [21]. It is interesting to note that the particular class of normalized one-side stable (Lévy) type of probabilities [38]

$$\psi(t) = \frac{\tau^\theta}{\Gamma(\theta)} t^{-1-\theta} \exp(-\tau/t), \qquad \text{with} \quad \tau > 0, \quad t > 0, \quad \theta > 0, \tag{B.1}$$

are solutions to a class of fractional differential equations of the Abel type [39]. In particular it is simple to see that the integer q-moments of the random variable t are finite if $\theta > q$. From now on let us refer to an Abel distribution in honour of the great mathematician. The Laplace transform of the probability density (B.1) can be calculated straightforwardly and reads:

$$\hat{\psi}(u) = \frac{2}{\Gamma(\theta)} (\sqrt{u\tau})^\theta K_\theta(2\sqrt{u\tau}), \tag{B.2}$$

where $K_\theta(z)$ is the Basset function [21]. Therefore using,

$$K_\theta(x) \simeq \frac{\Gamma(\theta) x^{-\theta}}{2^{1-\theta}} + \frac{\Gamma(-\theta) x^\theta}{2^{1+\theta}}, \qquad 0 < \theta < 1, \quad x \sim 0,$$

it follows that the asymptotic behaviour of $\hat{\psi}(u \sim 0)$ is given by

$$\hat{\psi}(u \sim 0) \simeq 1 - \frac{\pi \csc(\pi\theta)}{\theta \Gamma(\theta)^2} (\tau u)^\theta + \cdots, \qquad \text{with} \quad \theta \in (0, 1),$$

which is of the form (14). The interesting point is to mention that (B.2) allows us to study, for all u, waiting-time models of strong disorder, and in addition we can 'reduce' the disorder strength by increasing θ, i.e., depending on the value of θ we can obtain non-divergent integer moments of the random waiting times

$$\langle t^q \rangle = \int_0^\infty t^q \psi(t)\, \mathrm{d}t = \tau^q \frac{\Gamma(\theta - q)}{\Gamma(\theta)}, \qquad \text{if} \quad \theta > q. \tag{B.3}$$

Using Abel's model of waiting-time density $\psi(t)$, the memory kernel in the Laplace representation adopts the expression (see equation (7))

$$\hat{\mathbf{\Lambda}}(u) = \frac{u(\sqrt{\tau u})^\theta K_\theta(2\sqrt{\tau u})}{\frac{\Gamma(\theta)}{2} - (\sqrt{\tau u})^\theta K_\theta(2\sqrt{\tau u})}, \qquad \text{with} \quad \theta > 0. \tag{B.4}$$

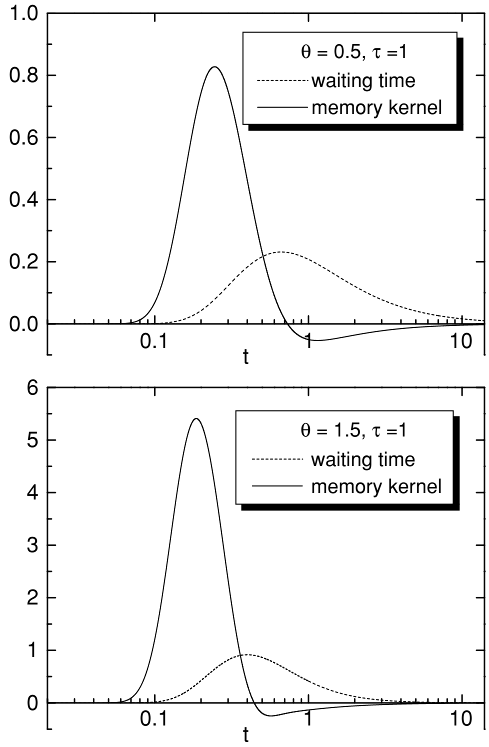

Figure 8. Typical temporal behaviour (in dimensionless time) of the memory kernel $\Lambda(t)$ using the Abel probability distribution (B.1) to characterize the strong disorder for different θ and $\tau = 1$. The memory kernel is not always positive and shows a maximum; note that in the case $1 < \theta < 2$ the kernel shows a sharper peak leading to a well-defined first moment. The plot also shows the corresponding waiting-time probability densities $\psi(t)$.

From the properties of the Laplace transform it is possible to check that for this model of strong disorder the area of the memory kernel is null, i.e., $\hat{\mathbf{\Lambda}}(u = 0) = 0$. Also the short- and long-time limits are simple to obtain:

$$\mathbf{\Lambda}(t = 0) = \lim_{u\to\infty} u\hat{\mathbf{\Lambda}}(u) \to 0^+,$$

and

$$\mathbf{\Lambda}(t = \infty) = \lim_{u\to 0^+} u\hat{\mathbf{\Lambda}}(u) \to 0^+.$$

After taking the Laplace inverse of (B.4), in figure 8 we have shown some typical cases for the memory kernel $\mathbf{\Lambda}(t)$, for $\theta = 1/2$ (all integer moments diverge) and $\theta = 3/2$ (only the first moment is finite). In addition we have also plotted the corresponding Abel densities $\psi(t)$.

References

[1] Bouchaud J P and Georges A 1990 *Phys. Rep.* **195** 127

[2] Sahimi M 1993 *Rev. Mod. Phys.* **65** 1393

[3] van Kampen N G 1992 *Stochastic Process in Physics and Chemistry* 2nd edn (Amsterdam: North-Holland)

[4] Metzler R and Klafter J 2004 *J. Phys. A: Math. Gen.* A **37** R161
Margolin G and Berkowitz B 2004 *Physica* A **334** 46–66
[5] Chen Z X and Yau J 1987 *Transp. Porous Media* **2** 145
[6] Hestir K and Long J C S 1990 *J. Geophys. Res.* **95** 21565
[7] Compte A and Caceres M O 1998 *Phys. Rev. Lett.* **81** 3140
[8] Haus J W and Kerh K W 1987 *Phys. Rep.* **150** 263, and references therein
[9] Cáceres M O, Schnorer H and Blumen A 1990 *Phys. Rev.* A **42** 4462
[10] Weiss G H 1994 *Aspect and Applications of the Random Walk* (Amsterdam: North-Holland), and references therein
[11] Monthus C 2004 *Phys. Rev.* E **69** 026103
[12] Bustingorry S, Reyes E R and Cáceres M O 2000 *Phys. Rev.* E **62** 7664
[13] Hernández-García E, Rodríguez M A, Pesquera L and San Miguel M 1990 *Phys. Rev.* B **42** 10653
[14] Hernández-García E and Cáceres M O 1990 *Phys. Rev.* A **42** 4503
[15] Pury P A, Cáceres M O and Hernández-García E 1994 *Phys. Rev.* A **49** R967
[16] Cáceres M O 2003 *Elementos de estadística de no equilibrio y sus aplicaciones al transporte en medios desordenados* (Barcelona: Reverté S.A.)
[17] Cáceres M O 2004 *Phys. Rev.* E **69** 036302
[18] Montroll E W and Scher H 1973 *J. Stat. Phys.* **9** 101
[19] Scher H and Montroll E W 1975 *Phys. Rev.* B **12** 2455 (see appendix D)
[20] Honig G and Hirdes U 1984 *J. Comp. Appl. Math.* **10** 113
[21] Sapnier J and Oldham K B 1987 *An Atlas of Functions* (Berlin: Springer)
[22] Hughes B D and Sahimi M 1993 *Phys. Rev.* E **48** 2776
[23] Deans H A 1963 *Soc. Pet. Eng. J.* **3** 49
[24] Coats K H and Smith B D 1964 *Soc. Pet. Eng. J.* **4** 73
[25] Bouchaud J P and Georges A 1988 *C. R. Acad. Sci., Paris* II **307** 1431, see also page 245 of [1]
[26] Landman U, Montroll E W and Shlesinger M F 1977 *Proc. Natl Acad. Sci. USA* **74** 430
Landman U and Shlesinger M F 1979 *Phys. Rev.* B **19** 6207
[27] Matheron G and de Marsily G 1980 *Water Resour. Res.* **16** 901
[28] Berkowitz B and Scher H 1997 *Phys. Rev. Lett.* **79** 4038
[29] Scher H *et al* 2002 *Geophys. Res. Lett.* **29** 1061
Dentz M, Cortis A, Scher H and Berkowitz B 2004 *Adv. Water Res.* **27** 155–73
[30] Somaruga C A 1999 Flujo de Trazadores en Reservorios de Petróleo Sometidos a Recuperación Secundaria *Master Tesis en Ing. Quim.* PLAPIQUI, Universidad Nacional del Sur, Bahía Blanca, Argentina
[31] Cáceres M O, Insua G L and Reyes E R, unpublished
[32] Ré M A and Budde C E 2000 *Phys. Rev.* E **61** 1110
[33] Bendler J T and Shlesinger M 1985 *The Wonderful World of Stochastics* ed M F Shlesinger and G H Weiss (Amsterdam: Elsevier)
[34] Lax M and Scher H 1977 *Phys. Rev. Lett.* **39** 781
[35] Montroll E W 1969 *J. Math. Phys.* **10** 753
[36] Pury P A and Cáceres M O 2002 *Phys. Rev.* E **66** 021112
[37] Abel N H 1823 Solution de quelques problems à l'aide d'integrales définies *Werke* **1** 10
[38] Eliazar I and Klafter J 2004 *Physica* A **336** 219
[39] Budini A A and Caceres M O 2004 *J. Phys. A: Math. Gen.* **37** 5959