Anomalous hydrodynamical dispersion and the transport with multiple families of paths in porous media

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We investigate a family of probability distributions that shows anomalous hydrodynamic dispersion, by solving a particular class of coupled generalized master equations. The Fourier-Laplace solution is obtained analytically in terms of the matrix Green function method; then the Coats-Smith concentration profile is revisited in a particular case. Two models of disorder are worked out explicitly, and the mean current is asymptotically calculated. We present an approximation method to calculate the first passage time distribution for this stochastic transport process, and as an example an exact Markovian result is worked out; scaling results are also shown. We discuss the comparison with other different methods to work out complex diffusion phenomena in the presence of disordered multiple transport paths. Extensions when the models are nondiffusive can also be solved in the Fourier-Laplace representation.

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I. INTRODUCTION

Hydrodynamic dispersion—dynamic convective mixing of two miscible fluids assisted by molecular diffusion [1]—is an important phenomenon relevant to secondary oil recovery, chemical packed-bed reactors, pollution of soil and ground water aquifers by nuclear wastes, etc. Thus, hydrodynamic dispersion has become—for some years now—a subject of great interest in many areas of science and engineering.

If a porous medium is macroscopically homogeneous, then the concentration profile of a solute mixing with a solvent by dispersion should be Gaussian at long times. However, many experimental data indicate significant deviations from a normal distribution. This is sometimes refereed to as *anomalous dispersion*. It is well known that most natural porous media, such as oil reservoirs, contain 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 by Deans [2] and Coats and Smith [3] in order to explain the origin of anomalous dispersion. These authors developed a semiempirical model to account for the anomalous hydrodynamics dispersion.

The Coats-Smith model is a one-dimensional convective-diffusion equation (CDE) which reproduces the effects of transient anomalous transport on the concentration profile C_f, by introducing a *transient loss term* in the CDE proportional to the rate of the concentration in the stagnant C_s, or dead-end volume, i.e.,

$$\frac{\partial C_f}{\partial t} = -\frac{\partial C_s}{\partial t} - V\frac{\partial C_f}{\partial x} + D_L\frac{\partial^2 C_f}{\partial x^2}, \tag{1}$$

here V is the macroscopic mean velocity of the flow and D_L is the longitudinal dispersion coefficient. Then the rate $\partial C_s/\partial t$ is characterized by a mass transfer coefficient K_c of the form

$$\frac{\partial C_s}{\partial t} = K_c(C_f - C_s), \tag{2}$$

and K_c^{-1} can be interpreted as the time that the fluid particles spend in the stagnant regions.

The Coats-Smith-Baker [4] model is a little more sophisticated; it is sometimes assumed that a fraction f of the pore volume is available for the flow, while $(1-f)$ is the stagnant fraction; so f and K_c are treated as adjustable parameters to fit the data. Using the Coats-Smith-Baker model, and suitable boundary conditions, Bacri *et al.* [5] attribute the transient anomalous dispersion in their data to the fact that the length of their experimental setup was too short to allow for the development of Gaussian dispersion. Nevertheless, using the same model Gist *et al.* [6] attributed the anomalous effect, in their experiment, to the heterogeneous nature of their porous medium. Thus, as was remarked by Sahimi [1], it is important to understand why the Coats-Smith model is able to provide such a good fit to the data. However, the origin of the anomalous transient in the concentration profile is yet a controversial question.

In this work we revisit the Coats-Smith equation from a mesoscopic point of view in an attempt to address the last question. Particularly, starting from a master equation—to describe the presence of multiple transport paths— and taking into account the disorder effect into the corresponding *transition* and *exchange* matrices, we have been able to revisit the Coats-Smith equation in its lattice versions. Then we can go one step further and generalize the Coats-Smith model in n dimensions and consider generalized non-Fickian operators for each disordered multiple transport path. This generalization gives the possibility of understanding the me-

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soscopic nature of the Coats-Smith model and tackling a new range of transport problems which are outside of the scope of the Coats-Smith equation; for example, we could work out the problem of flow transport in stratified and disordered porous media with fractures.

The outline of the paper is as follows. In Sec. II, we present a generalized master equation with an internal state (for a given realization of the disorder) that describes the system of interest, i.e., we use the theory of the multistate continuous time random walk (MCTRW) [7,8] to tackle the problem of complex transport phenomena in random systems and in the presence of convection and multiple path options. The description of the models of disorder, employed in our studies [9,10], and the comparison with the Coats-Smith equation and their generalizations are given in Secs. II A and II B. The solution for the concentration profiles (probability distributions) averaged over the disorder is presented in terms of the matrix Green function method in Sec. III; also in Sec. III A two applications are presented, in particular, we show—for two different models of disorder—the asymptotic temporal behavior of the current (i.e., the response to the injection of an initial pulse); in Sec. III B we apply our method to calculate the exact solution of the Coats-Smith profile. The theory of the first passage time distribution with internal states is presented in Sec. IV; in Sec. IV A we apply this approach to calculate a Markovian exact result and to present scaling results. Finally, in Sec. V, we briefly summarize the results of our work and present our future programs. Appendix A is devoted to the calculation of the average over the disorder, and in Appendix B we show an alternative study of the first passage time distribution for stochastic processes with internal states.

II. MODELING A MASTER EQUATION WITH DISORDERED MULTIPLE TRANSPORT PATHS

Recently it has been remarked that simple descriptions in terms of *single* distributions are totally inadequate to describe the flow transport in rocks consisting of interconnected and intertwined networks of fractures and pores [11,12]; then it was suggested that, in general, the starting point to study this type of complex transport phenomena (such as transport in polycrystal, porous catalysts, coalbed methane reservoirs, geological systems with fractures and pores, etc.) should be done in terms of a master equation with multiple families of transport paths [13]. In that reference the disorder was considered in both the *transition* matrix of the random walk and the *exchange* matrix which gives the rate of transition between different transport paths at a given site. Hughes and Sahimi [13] introduced the average over the disorder using a sort of effective medium approximation (EMA) with internal states. Many different models of disorder were solved, but the general case in which both *transition* and *exchange* disorder are present was not tackled due to the great complexity of the algebra [14]. Here we are going to bypass this difficulty by introducing an alternative procedure to take the average over the disorder; this is, in principle, a useful approximation for the calculation of the mean probability distributions. As a bonus, and for a special case of disorder we recover the Coats-Smith equation, so we can immediately generalize this equation to many different interesting physical situations.

Let $R_l(j,t)$ be the probability that a walker arrives at site j on path l *just* at time t. Then the functions $R_l(j,t)$ obey the following continuous-time recurrence relations [8,15]:

$$R_l(j,t)=\sum_{j'}\sum_{l'}\int_0^t \Psi_{ll'}(j,j',t-\tau)\,R_{l'}(j',\tau)\,d\tau + \delta(t)\,\delta_{j0}\,c_l \quad \text{with} \quad 0\leqslant c_l\leqslant 1, \tag{3}$$

where the elements $\Psi_{ll}(j,j',t)$ of the matrix transition probability density are associated with the jump of a walker on path l from site j' to j after a waiting time t. The starting point to describe a MCTRW [16] is the characterization of the *waiting-time* matrix Ψ. Consider, for example, a system with two possible transport paths B and A (its generalization to N possible transport paths is obvious), then for a fixed realization of the disorder we can write [9,10,17]

$$\Psi=\begin{pmatrix} B_{ij}\exp\left(-t\sum_m B_{mj}\right)\phi_j^B(t) & \delta_{ij}\exp\left(-t\sum_m A_{mj}\right)\psi_j^{BA}(t) \\ \delta_{ij}\exp\left(-t\sum_m B_{mj}\right)\psi_j^{AB}(t) & A_{ij}\exp\left(-t\sum_m A_{mj}\right)\phi_j^B(t) \end{pmatrix}, \tag{4}$$

where B_{ij} is the *transition* probability rate (in the path B) from site j to i. $\exp(-t\Sigma_m B_{mj})$ is the probability that no jump (along the path B) to another site has occurred up to time t after the last step (i.e., the *sojourn* probability at site j into the path B). $\phi_j^B(t)$ is the probability that the walker does not leave (from site j) the path B during the time interval t since the last step. $\psi_j^{AB}(t)\,dt$ is the *exchange* probability (at site j) at time $t+dt$ from path B to A.

Similar definitions follow for the *transition* and *exchange* components along path A; for example, A_{ij} is the *transition* probability rate (in path A) from site j to i, etc. [19].

Note that the integral in time and sum over sites of any

column of Ψ gives 1, this indicates that the *waiting-time* matrix is properly defined (the MCTRW is well normalized); for example, for column 1 we get

$$\mathcal{I}=\int_0^\infty \sum_i B_{ij}\exp\left(-t\sum_m B_{mj}\right)\phi_j^B(t)\,dt + \int_0^\infty \sum_i \delta_{ij}\exp\left(-t\sum_m B_{mj}\right)\psi_j^{AB}(t)\,dt = \int_0^\infty \exp\left(-t\sum_m B_{mj}\right)\left(\sum_i B_{ij}\,\phi_j^B(t)+\psi_j^{AB}(t)\right)dt.$$

Defining $\beta_j \equiv \Sigma_m B_{mj}$ it is simple to prove that $\mathcal{I}=1$; this is so because

$$\mathcal{I}=\beta_j\int_0^\infty e^{-\beta_j t}\phi_j^B(t)\,dt+\int_0^\infty e^{-\beta_j t}\psi_j^{AB}(t)\,dt = \beta_j\,\mathcal{L}_{\beta_j}[\phi_j^B(t)]+\mathcal{L}_{\beta_j}[\psi_j^{AB}(t)],$$

where $\mathcal{L}_u[f(t)]\equiv\hat{f}(u)$ indicates the Laplace transform of any function $f(t)$. In general, using that $\phi(t)=1-\int_0^t\psi(t')\,dt'$, it follows that $\hat{\phi}(u)=(1-\hat{\psi}(u))/u$, then the proof follows immediately.

The key element in the continuous time random walk (CTRW) theory is the calculation of the effective *waiting-time* function [20,21]. As in the CTRW theory, in the context of the MCTRW the effective *waiting-time* matrix is defined taking the average—over the disorder—of its elements. Therefore in the same spirit of the CTRW [22] (see Appendix A) we introduce here the following (Hartree) approximation; for example, to calculate the average of elements Ψ_{11} and Ψ_{21},

$$\langle\Psi_{11}\rangle_{\text{Disorder}}\equiv\left\langle B_{ij}\exp\left(-t\sum_m B_{mj}\right)\phi_j^B(t)\right\rangle \simeq\left\langle B_{ij}\exp\left(-t\sum_m B_{mj}\right)\right\rangle\langle\phi_j^B(t)\rangle, \quad (5)$$

$$\langle\Psi_{21}\rangle_{\text{Disorder}}\equiv\left\langle \delta_{ij}\exp\left(-t\sum_m B_{mj}\right)\psi_j^{AB}(t)\right\rangle \simeq\left\langle \delta_{ij}\exp\left(-t\sum_m B_{mj}\right)\right\rangle\langle\psi_j^{AB}(t)\rangle. \quad (6)$$

Similar expressions follow for the other components $\langle\Psi_{ll'}\rangle$. The crucial point in a CTRW theory is to assume that after taking the average, the system is homogeneous in space and is characterized by a translational invariant transition function $\lambda(i-j)$ in a regular lattice; then the disorder is modeled by considering different *waiting-time* functions $\psi(t)$. The same happens with the MCTRW theory in the presence of internal states. Then after taking the average over the disorder we define the following functions that characterize the lattice *transition* into each path *B* and *A*, respectively (for the separable case):

$$\left\langle B_{ij}\exp\left(-t\sum_m B_{mj}\right)\right\rangle=\lambda_1(i-j)\;\psi_1^T(t),$$

$$\left\langle A_{ij}\exp\left(-t\sum_m A_{mj}\right)\right\rangle=\lambda_2(i-j)\;\psi_2^T(t).$$

Consequently the functions $\phi_l^T(t)\equiv 1-\int_0^t\psi_l^T(t')\,dt'$ (sojourn) are defined by

$$\left\langle \delta_{ij}\exp\left(-t\sum_m B_{mj}\right)\right\rangle=\phi_1^T(t),$$

$$\left\langle \delta_{ij}\exp\left(-t\sum_m A_{mj}\right)\right\rangle=\phi_2^T(t).$$

In the same way the *exchange* between paths is characterized by the *waiting-time* functions

$$\langle\psi_j^{AB}(t)\rangle=\psi_{21}^E(t),$$

$$\langle\psi_j^{BA}(t)\rangle=\psi_{12}^E(t),$$

and consequently the functions $\phi_l^E(t)\equiv 1-\int_0^t\psi_{l'l}^E(t')\,dt'$ are defined by

$$\langle\phi_j^B(t)\rangle=\phi_1^E(t),$$

$$\langle\phi_j^A(t)\rangle=\phi_2^E(t).$$

Note that after taking the average over the disorder we assume that $\psi_{ll'}^E(t)$ and $\phi_l^E(t)$ are homogeneous in space.

With all these functions, we can immediately write down the Fourier transform of the effective *waiting-time* matrix $\langle\Psi\rangle_{\text{Disorder}}\equiv\eta(k,t)$ in the form

$$\eta(k,t)\equiv\begin{pmatrix}\eta_{11}&\eta_{12}\\ \eta_{21}&\eta_{22}\end{pmatrix} =\begin{pmatrix}\lambda_1(k)\;\psi_1^T(t)\;\phi_1^E(t) & \phi_2^T(t)\;\psi_{12}^E(t)\\ \phi_1^T(t)\;\psi_{21}^E(t) & \lambda_2(k)\;\psi_2^T(t)\;\phi_2^E(t)\end{pmatrix}. \quad (7)$$

Here it is important to remark that a Markovian evolution will appear if and only if all the *waiting-time* functions are exponential. A typical *waiting-time* function is shown in Appendix A; in particular, in that appendix we calculate a possible *exchange* waiting time assuming a model of strong disorder for the *exchange* probability (at site j) from path *B* to *A*.

The general solution of our MCTRW process can be given in terms of the matrix Green function (see the following section). But, before going ahead with this program, let us introduce here the corresponding generalized master equation associated with the MCTRW characterized by the *waiting-time* matrix (7). Doing this we will be able to establish the connection between the propagator of the MCTRW process and the one from the Coats-Smith equation.

A. Computing the generalized master equation

Let $P_l(k,t)$ be the Fourier transform of the probability in path l and time t. Then the evolution equation governing these elements is of the form (note that the Fourier transform is taken over the lattice space) of a generalized master equation with internal states [18]

$$\partial_t P_l(k,t) = \int_0^t \sum_{l''} \Lambda_{ll''}(k,t-\tau)\, P_{l''}(k,\tau)\, d\tau - \int_0^t P_l(k,\tau) \sum_{l''} \Lambda_{l''l}(k=0,\, t-\tau)\, d\tau. \quad (8)$$

The interesting point is knowing the relation between the elements $\Lambda_{ll''}(k,t)$ and the elements of the *waiting-time* matrix $\boldsymbol{\eta}_{ll''}(k,t)$. This connection is well established [20,21,23], in particular, the Fourier-Laplace representation is given by

$$\hat{\Lambda}_{ll'}(k,u) = \frac{u\ \hat{\eta}_{ll'}(k,u)}{1-\sum_{l''}\ \hat{\eta}_{l''l'}(k=0,u)}. \quad (9)$$

Thus we can rearrange Eq. (8) to show the explicit structure of its elements. Using Eq. (7), we see that only the diagonal elements of Eq. (9) are k dependent. For the component $l=1$ we have

$$\partial_t P_1(k,t) = \int_0^t [\Lambda_{11}(k,t-\tau) - \Lambda_{11}(k=0,\, t-\tau)]\, P_1(k,\tau)\, d\tau - \int_0^t \Lambda_{21}(t-\tau)\, P_1(k,\tau)\, d\tau + \int_0^t \Lambda_{12}(t-\tau)\, P_2(k,\tau)\, d\tau, \quad (10)$$

and for the component $l=2$ we have

$$\partial_t P_2(k,t) = \int_0^t [\Lambda_{22}(k,t-\tau) - \Lambda_{22}(k=0,\, t-\tau)]\, P_2(k,\tau)\, d\tau + \int_0^t \Lambda_{21}(t-\tau)\, P_1(k,\tau)\, d\tau - \int_0^t \Lambda_{12}(t-\tau)\, P_2(k,\tau)\, d\tau, \quad (11)$$

where

$$\hat{\Lambda}_{l'l}(u) = \frac{u\, \mathcal{L}_u[\,\phi_l^T(t)\,\psi_{l'l}^E(t)]}{1-\mathcal{L}_u[\,\phi_l^T(t)\,\psi_{l'l}^E(t)] - \mathcal{L}_u[\lambda_l(k=0)\,\psi_l^T(t)\,\phi_l^E(t)]} \quad \text{for } l\neq l', \quad (12)$$

$$\hat{\Lambda}_{ll}(k,u) = \frac{u\,\lambda_l(k)\,\mathcal{L}_u[\,\psi_l^T(t)\,\phi_l^E(t)]}{1-\mathcal{L}_u[\,\phi_l^T(t)\,\psi_{l'l}^E(t)] - \mathcal{L}_u[\lambda_l(k=0)\,\psi_l^T(t)\,\phi_l^E(t)]}.$$

From Eq. (12) we may describe a great diversity of physical situations, and while in fact this has been known for many years in the literature of statistical physics, it seems to me that it has not yet been fully explored in the area of fluid physics. Just in order to clarify this point let us revisit the Coats-Smith equation from our mesoscopic point of view.

The Coats-Smith equation revisited

Here we would like to remark that if there is no disorder, Eqs. (5) and (6) are exact results and the *waiting-time* functions must be exponential functions. On the other hand, if the disorder is weak (it means that the kinetic coefficients are renormalized quantities but the universal laws remain unchanged) the *waiting-time* functions can be approximated to be exponential, perhaps with different coefficients in order to characterize the different time scales involved in the process (see Appendix A). Therefore let us assume that the *transition waiting-time* functions involved in Eq. (12) are all exponential. In order to get an explicit result we choose the functions

$$\psi_l^T(t) = \alpha_l \exp(-\alpha_l t), \quad (13)$$

then the associated sojourns are given by

$$\phi_l^T(t) = \exp(-\alpha_l t). \quad (14)$$

From Eqs. (13) and (14), and taking the Laplace transform involved in Eq. (12), after using the known relation $\mathcal{L}_u[e^{-at}f(t)] = \hat{f}(u+a)$, it is simple to see that the off-diagonal elements are the ones responsible of the *exchange* between paths

$$\hat{\Lambda}_{l'l}(u) = \frac{\hat{\psi}_{l'l}^E(u+\alpha_l)}{\hat{\phi}_l^E(u+\alpha_l)} \quad \text{for } l\neq l'. \quad (15)$$

On the other hand, the diagonal elements give rise to the transport operators into each corresponding path, i.e.,

$$\hat{\Lambda}_{ll}(k,u) = \alpha_l\,\lambda_l(k). \quad (16)$$

Now we also assume that the *exchange waiting times* are exponential (weak disorder in the Markovian approximation, see Appendix A),

$$\psi_{l'l}^E(t) = \nu_{l'l} \exp(-\nu_{l'l} t), \quad (17)$$

then the associated sojourns are given by

$$\phi_l^E(t) = \exp(-\nu_{l'l} t). \quad (18)$$

Thus in the Laplace representation, from Eq. (15) we immediately arrive at the following expressions:

$$\hat{\Lambda}_{l'l}(u) = \nu_{l'l} \quad \text{for } l\neq l'. \quad (19)$$

As expected, there are no memory effects neither in the *exchange* nor in the *transition* matrices of the coupled master equation [the inverse Laplace transform of Eqs. (16) and (19) is of the form $\mathcal{L}^{-1}(\text{constant})=\text{const}\,\delta(t)$]; this means that the MCTRW process is a Markovian one. So from Eqs. (16) and (19), after taking the inverse Laplace transform, we arrive at the following coupled master equations (in its Fourier representation):

$$\partial_t P_1(k,t)=\alpha_1[\lambda_1(k)-1]P_1(k,t)-\nu_{21}P_1(k,t)+\nu_{12}P_2(k,t), \tag{20}$$

$$\partial_t P_2(k,t)=\alpha_2[\lambda_2(k)-1]P_2(k,t)+\nu_{21}P_1(k,t)-\nu_{12}P_2(k,t).$$

Again, we immediately get back the Coats-Smith equation (in its lattice version) if we assume the probabilities $P_l(k,t)$ to be proportional to the concentration rates, $C_l(k,t)/C_l(k,0)$. Therefore from Eq. (20) taking $\lambda_2(k)\to 1$ and the Fourier representation of the convection-diffusion operator to be $\alpha_1[\lambda_1(k)-1]$, and $\nu_{21}=\nu_{12}=K_c$, we arrive at the Fourier version of the Coats-Smith equation. This result means that the presence of disorder (in the Markovian approximation) does not change the structure of the Coats-Smith equation, and gives the same evolution equation as in a homogeneous (ordered) system. Thus we have shown that the Coats-Smith model arises from the mesoscopic description of complex transport in the presence of multiple transport paths in a Markovian approximation; this result is in agreement with the idea of multiple transport paths in complex media [13], or composite Markov processes [18].

Note that, in general, in Eq. (20) the presence of a lattice-Fickian operator $[\lambda_2(k)-1]$ allows for diffusion also in path *A*, this fact gives us the possibility to consider the case when the concentration in the stagnant regions can diffuse over a very long time scale α_2^{-1}.

In order to exemplify that the Fourier representation of Eqs. (1) and (2) corresponds to our Eq. (20) it is still necessary to give the *transition* lattice structure function $\lambda_1(k)$. From this program it will be trivial to see that our Eq. (20) may be generalized to a Coats-Smith equation in *n* dimensions. Consider, for example, a two-dimensional lattice where the macroscopic Darcy flow velocity *V* points along the direction $\hat{x}$. The lattice structure is given by

$$\lambda_1(k)=\sum_r \exp(ik\cdot r)\,\lambda(r-r').$$

Because the lattice vector *r* is translational invariant, and considering that the one-step (elemental) next-neighborhood transitions (in a simple square lattice) are characterized by a probability to jump to the right (left), $p_x(q_x)$, and a probability to jump up (down), $p_y(q_y)$, we get for the lattice structure the function

$$\begin{aligned}\lambda_1(k_x,k_y)&=p_x e^{ik_x a}+q_x e^{-ik_x a}+p_y e^{ik_y a}+q_y e^{-ik_y a}\\&=2p_y\cos(k_y a)+(1-2p_y)\cos(k_x a)\\&\quad -i(1-2p_y-2p_x)\sin(k_x a),\end{aligned} \tag{21}$$

where *a* is the lattice parameter and $1=p_x+q_x+p_y+q_y$; in the second line we have used that $p_y=q_y$; so we can identify a mean velocity flow *V*. To see this more easily, take the limit of small lattice parameter *a*. Then

$$\lambda_1(k_x,k_y)\simeq 1-i(1-2p_y-2p_x)(k_x a)-2p_y\frac{(k_y a)^2}{2}-(1-2p_y)\frac{(k_x a)^2}{2}+\cdots. \tag{22}$$

This means that $2p_y a^2\propto D_\perp$ (transverse dispersion coefficient), $(1-2p_y)a^2\propto D_L$ (longitudinal dispersion coefficient), and the mean velocity flow is characterized by $(-1+2p_y+2p_x)a\propto V$. Of course, from the present *lattice* Coats-Smith version (20), more general situations can also be taken into account. This is a nontrivial result that is hard to get in the context of the EMA theory; see, for example, Ref. [24] where we have been able to solve an asymmetric anisotropic disordered media in the context of EMA (but without internal states). In the following section we leave, for a moment, the discussion about the lattice structure $\lambda_1(k_x,k_y)$, to get into the more interesting matter concerning memory effects in a generalized Coats-Smith equation (due to the presence of disorder).

B. The generalized Coats-Smith equation

In this section we explicitly use the fact that there is no transport in the path *A*; then as before we assume in Eq. (4) that $A_{ij}=0$. This implies that $\lambda_2(k)=1$ and $\phi_2^T(t)=1$. So from Eq. (7) the matrix $\eta(k,u)$ will look like

$$\eta(k,t)=\begin{pmatrix}\lambda_1(k)\,\psi_1^T(t)\,\phi_1^E(t) & \psi_{12}^E(t)\\ \phi_1^T(t)\,\psi_{21}^E(t) & 0\end{pmatrix}. \tag{23}$$

In the present section we would like to comment on some situations which are in fact beyond the Coats-Smith model. Consider the case when the disorder produces a memory kernel in the *transition* and the *exchange* matrices. In this case the diagonal elements of the generalized master equation are

$$\hat{\Lambda}_{11}(k,u)=\frac{u\,\lambda_1(k)\mathcal{L}_u[\psi_1^T(t)\phi_1^E(t)]}{1-\mathcal{L}_u[\phi_1^T(t)\psi_{21}^E(t)]-\mathcal{L}_u[\psi_1^T(t)\phi_1^E(t)]},$$

$$\hat{\Lambda}_{22}(k,u)=0, \tag{24}$$

and the off-diagonal elements are given by

$$\hat{\Lambda}_{12}(u)=\frac{u\,\mathcal{L}_u[\psi_{12}^E(t)]}{1-\mathcal{L}_u[\psi_{12}^E(t)]}, \tag{25}$$

$$\hat{\Lambda}_{21}(u)=\frac{u\,\mathcal{L}_u[\,\phi_1^T(t)\psi_{21}^E(t)]}{1-\mathcal{L}_u[\,\phi_1^T(t)\psi_{21}^E(t)]-\mathcal{L}_u[\,\psi_1^T(t)\phi_1^E(t)]}.$$

This is the general case when no transport is allowed in path *A*; many particular situations can be analyzed considering different expressions for the *waiting-time* functions $\psi_l^T(t)$ and $\psi_{ll'}^E(t)$.

1. Mixing strong disorder and weak disorder

Consider the case when the strong disorder is present only in the *transition* waiting time. This case corresponds to the situation when

$$\psi_l^T(t)=\text{arbitrary},$$

$$\psi_{ll'}^E(t)=\text{exponential}.$$

Using the exponential model (17), from Eqs. (24) and (25) we arrive to the following elements $\hat{\Lambda}_{ll'}(k,u)$:

$$\hat{\Lambda}_{11}(k,u)=\lambda_1(k)\frac{\hat{\psi}_1^T(u+\nu_{21})}{\hat{\phi}_1^T(u+\nu_{21})},\quad \hat{\Lambda}_{22}(k,u)=0, \tag{26}$$

$$\hat{\Lambda}_{12}(u)=\nu_{12},\quad \hat{\Lambda}_{21}(u)=\nu_{21}. \tag{27}$$

Due to the shift in the Laplace argument of $\hat{\Lambda}_{11}(k,u)$, there will not be a long-time anomalous effect in the evolution of the process; even in the case when $\hat{\psi}_1^T(u)$ is not analytic around $u=0$. Note that the Laplace structure of the element $\hat{\Lambda}_{11}(k,u)$ will drive to a transient memory effect at short times, of the order of ν_{21}^{-1}, even if $\psi_1^T(t)$ were exponential.

Consider now the case when the strong disorder is only present in the *exchange* waiting time. This case corresponds to the situation when

$$\psi_l^T(t)=\text{exponential},$$

$$\psi_{ll'}^E(t)=\text{arbitrary}.$$

Suppose, for example, the symmetrical case $\hat{\psi}_{12}^E(u)=\hat{\psi}_{21}^E(u)=\hat{\psi}^E(u)$, and in addition that $\hat{\psi}^E(u)$ represents the presence of strong disorder (see Appendix A). Then $\hat{\psi}^E(u)$ must be a nonanalytic function of the Laplace variable in $u=0$. A possible representation for small u is

$$\hat{\psi}^E(u)=(1+Cu^\theta)^{-1}\quad \text{with}\quad 0<\theta<1, C=\text{const}. \tag{28}$$

We see that for very long times (in the Laplace representation $u\sim 0$): $\hat{\psi}^E(u)\sim(1-Cu^\theta)$, this fact leads to a long-tail distribution with a divergent mean waiting time. From Eqs. (28) and (25) it is simple to show that $\hat{\Lambda}_{12}(u)=u^{1-\theta}/C$. In general, from Eqs. (24), (25), and (13) it follows that the elements $\hat{\Lambda}_{ll'}(k,u)$ are

$$\hat{\Lambda}_{11}(k,u)=\alpha_1\lambda_1(k),\quad \hat{\Lambda}_{22}(k,u)=0, \tag{29}$$

$$\hat{\Lambda}_{12}(u)=u^{1-\theta}/C,\quad \hat{\Lambda}_{21}(u)=\frac{\hat{\psi}^E(u+\alpha_1)}{\hat{\phi}^E(u+\alpha_1)}. \tag{30}$$

As before, due to the shift in the Laplace argument of $\hat{\Lambda}_{21}(u)$, there will not be a long-time anomalous effect in this element, even in the case when $\hat{\psi}_1^E(u)$ is not analytic around $u=0$ as in Eq. (28). This model corresponds to considering strong disorder in the *exchange* matrix, but a Markovian approximation in the *transition* matrix. Physically this means that changing the paths, at any site *j*, are rare events; on the other hand, the disorder only introduces a renormalization in the kinetic coefficients of the transport operator into the path *B*. As mentioned before, assuming $\psi_1^T(t)=\alpha_1\exp(-\alpha_1 t)$, and the expression for the *exchange* waiting time (28) it is possible to see that the asymptotic long-time expression for the elements $\Lambda_{ll'}(k,t-\tau)$ is given by

$$\Lambda(k,t-\tau)\simeq\begin{pmatrix}\alpha_1\lambda_1(k)\,\delta(t-\tau) & C_2/(t-\tau)^{2-\theta}\\ C_1\delta(t-\tau) & 0\end{pmatrix}, \tag{31}$$

where C_1 and C_2 are constants. Thus the long-time evolution equation that governs the concentration profile can be read from Eqs. (10) and (11) considering the memory (31). This result predicts that there will be long tails for the long time regime. Note that we have used that the Laplace shift in the argument of $\hat{\Lambda}_{21}(u)$ removes the nonanalyticity coming from $\hat{\psi}^E(u)$.

To end this discussion consider here the case when the strong disorder is present in both: the *transition* operator, namely, into the path *B*, and in the *exchange* between paths. This case corresponds to the situation when

$$\psi_l^T(t)=\text{arbitrary},$$

$$\psi_{ll'}^E(t)=\text{arbitrary}.$$

If the disorder introduces nonanalytic expressions for the *transition* and the *exchange waiting times* (which might, for example, result from energetic or spatial disorder on the paths [10]), then long-memory kernels will appear in all the elements $\hat{\Lambda}_{ll'}(k,u)$. In this case, depending on the particular structure of each function $\psi_l^T(t)$ and $\psi_{ll'}^E(t)$, the elements $\hat{\Lambda}_{ll'}(k,u)$ can be nonanalytic in $u=0$. We would like to stress that if the memory functions $\hat{\Lambda}_{ll'}(k,u)$ are nonanalytic, this leads to the occurrence of a long-time anomalous behavior (long-time tails or asymptotic non-Gaussian profiles) in the concentration.

2. Extensions

Another interesting model is when we consider that the structure function, which characterizes the transport in a particular path *l*, has a nonseparable structure of the form $\hat{\psi}_l^T(k,u)$. This is just the case that appears when we study a dye in a steady flow through a fracture network [25]. Thus

the interesting case when multiple families of transport paths include the possibility of a fracture network in a porous rock, can also be analyzed by using the present approach; considering, for example, that the $\eta(k,t)$ matrix is given by

$$\eta(k,t)=\begin{pmatrix} \lambda_1^T(k)\psi_1^T(t)\ \phi_1^E(t) & \phi_2^T(t)\ \psi_{12}^E(t) \\ \phi_1^T(t)\ \psi_{21}^E(t) & \lambda_2^T(k,t)\ \phi_2^E(t) \end{pmatrix},$$

where, of course, $\phi_2^T(t)=1-\int_0^t \lambda_2^T(k=0,\tau)\,d\tau$.

It should be remarked that even when all these models of coupled master equations could look unwielding, we can work out their solution because we can map this process with a MCTRW one (see the following section).

III. COMPUTING THE MATRIX GREEN FUNCTION AND THE MOMENTS OF THE MCTRW PROCESS

In general, if we know the matrix $\hat{\eta}(k,u)$, we can solve the Fourier-Laplace transform of the probability $P_l(j,t)$ to be at site j in the path l at time t. The equation describing these probabilities is given by the relation [8,10,15,20,21,23]

$$P_l(j,t)=\int_0^t \Phi_l(t-\tau)\,R_l(j,\tau)\,d\tau, \tag{32}$$

where $\Phi_l(t)$ is the probability that in the interval of time $[0,\,t]$ no further jump occurred,

$$\Phi_l(t)=1-\sum_{j''}\sum_{l''}\int_0^t \eta_{l''l}(j'',\tau)\,d\tau. \tag{33}$$

Note that the solution of $R_l(j,\tau)$ can be found from Eq. (3) using $\Psi\to\eta$ and taking the Fourier-Laplace transform. As usual, we start with our walkers at origin; however, we allow them to be situated on different paths. The normalized initial condition is then

$$P_l(j,0)=\delta_{j0}\,c_l,$$

with $c_1+\cdots+c_N=1$ (N is the number of different paths). Notice that Eq. (32) is a convolution in time, which simplifies in the Laplace representation. Furthermore, for $\Phi_l(t)$ one has in the Laplace representation

$$\hat{\Phi}_l(u)=\frac{1-\sum_{j''}\sum_{l''}\hat{\eta}_{l''l}(j'',u)}{u}. \tag{34}$$

In the following we will use the vectorial notation

$$\hat{\mathbf{P}}(k,u)=[\hat{P}_1(k,u),\ldots,\hat{P}_N(k,u)]$$

and denote by $\mathbf{P}_0(k)$ the Fourier transform of the initial occupation probability $\mathbf{P}(j,t=0)$, i.e., $\mathbf{P}_0(k)\equiv\mathbf{P}(k,t=0)$. Here we are interested in a Green function, so we use the initial condition $\mathbf{P}_0(k)=\mathbf{P}_0$ independent of the Fourier variable k. The solution of the MCTRW in the Fourier-Laplace representation is well known [8,15,23]. For instance, use Eqs. (32) and (33) and the recurrence relation (3) in the Fourier-Laplace representation with $\hat{\eta}(k,u)=\mathcal{L}_u[\mathcal{F}_k[\langle\Psi\rangle_{\text{Disorder}}]]$; then

$$\hat{\mathbf{P}}(k,u)=\hat{\mathbf{\Phi}}(u)\cdot[\mathbf{1}-\hat{\eta}(k,u)]^{-1}\cdot\mathbf{P}_0, \tag{35}$$

where $\hat{\mathbf{\Phi}}(u)=[\delta_{ll'}\hat{\Phi}_l(u)]$ is a diagonal matrix, and $\hat{\eta}(k,u)$ is the Laplace transform of the matrix characterized in Eq. (7). Thus the matrix Green function is just $\hat{\mathbf{\Phi}}(u)\cdot[\mathbf{1}-\hat{\eta}(k,u)]^{-1}$. From this expression the determination of many quantities of interest is reduced to a Laplace inversion. For example, from Eq. (35) all the moments of the distribution $\mathbf{P}(j,t)$ can be easily calculated . One has (in one dimension)

$$\overline{j_l^m(t)}\equiv\sum_j j^m\,P_l(j,t)=(-i)^m\mathcal{L}^{-1}\left[\frac{\partial^m}{\partial k^m}\hat{P}_l(k,u)\right]_{k=0}.$$

Note that here, $\overline{j_l^m(t)}$ means a random walk average. Setting $\hat{\mathbf{\Theta}}\equiv[\mathbf{1}-\hat{\eta}(k,u)]^{-1}$, for example, the first and second moments can be written as

$$\overline{\hat{j}_l(u)}=-i\left[\hat{\mathbf{\Phi}}\cdot\hat{\mathbf{\Theta}}\cdot\frac{\partial\hat{\eta}}{\partial k}\cdot\hat{\mathbf{\Theta}}\cdot\mathbf{P}_0\right|_{k=0}\Bigg]_l,$$

$$\overline{\hat{j}_l^2(u)}=-\Bigg\{\hat{\mathbf{\Phi}}\cdot\Bigg[2\hat{\mathbf{\Theta}}\cdot\frac{\partial\hat{\eta}}{\partial k}\cdot\hat{\mathbf{\Theta}}\cdot\frac{\partial\hat{\eta}}{\partial k}\cdot\hat{\mathbf{\Theta}}+\hat{\mathbf{\Theta}}\cdot\frac{\partial^2\hat{\eta}}{\partial k^2}\cdot\hat{\mathbf{\Theta}}\cdot\mathbf{P}_0\Bigg]_{k=0}\Bigg\}_l.$$

It is now simple to show that the current in the path l is given, in the Laplace representation [10], just by

$$\hat{I}_l(u)=u\overline{\hat{j}_l(u)}=(-i)u\left[\hat{\mathbf{\Phi}}\cdot\hat{\mathbf{\Theta}}\cdot\frac{\partial\hat{\eta}}{\partial k}\cdot\hat{\mathbf{\Theta}}\cdot\mathbf{P}_0\right|_{k=0}\Bigg]_l. \tag{36}$$

These results show that many important quantities can be calculated straightforwardly from our approach; thus the study of the time transients is indeed reduced to the analysis of the inverse Laplace transform.

A. Applications (the current)

Here we shall use the matrix Green function method to calculate the current in a one-dimensional system in the presence of disordered multiple transport paths. In particular, we can analyze the hydrodynamics dispersion for an initial pulse condition (Dirac-δ), for two models of disorder, namely, when the strong disorder is in the *transition*, and when it is in the *exchange* matrix.

Let us start with the first case; then assuming that the transport only occurs in the path *B*, and that the strong-disorder is only present in the *transition* matrix (i.e., in the path *B*), see expressions (26) and (27). Thus the corresponding $\hat{\eta}(k,u)$ matrix is given by

$$\hat{\eta}(k,u)=\begin{pmatrix} \lambda_1(k)\,\psi_1^T(u+\nu_{21}) & \dfrac{\nu_{12}}{u+\nu_{12}} \\ \nu_{21}\phi_1^T(u+\nu_{21}) & 0 \end{pmatrix}, \tag{37}$$

where the (asymptotic) lattice-Fickian operator is given in terms of a Taylor expansion of the structure function [in one dimension use Eq. (22) with $p_y=q_y=0$],

$$\lambda_1(k_x)\simeq 1-i(1-2p_x)(k_x a)-\frac{(k_x a)^2}{2}+\cdots, \quad \text{with} \quad 0\leqslant p_x\leqslant 1. \tag{38}$$

In order to simplify the algebra, let us assume that the *exchange* rates are symmetric, then $\nu_{21}=\nu_{12}=K_c$; so the current in path B can easily be calculated using Eq. (37) in Eq. (36) with $l=1$. In this case the current (i.e., a quantity proportional to the mean velocity of the propagating pulse into the transport path B) is characterized by

$$\hat{I}_1(u)=\frac{(2p_x-1)(K_c+u)^{3-\theta}a}{C\,u\,(2K_c+u)^2} \quad \text{for} \quad 0<\theta<1, \tag{39}$$

where we have used the initial condition $\mathbf{P}_0=(1,0)$ and the nonanalytic *transition* waiting time $\psi_1^T(u)=(1+C\,u^\theta)^{-1}$. This expression gives (in the Laplace representation) both the transient and long-time behaviors of the current in the path B. For example, using the inverse Laplace theorem it is simple to show that for times $t\gg K_c^{-1}$ the temporal asymptotic behavior is a constant,

$$I_1(t)\simeq\frac{(2p_x-1)K_c^{1-\theta}a}{4C} \quad \text{with} \quad 0<\theta<1. \tag{40}$$

This means that asymptotically in time, the hydrodynamic dispersion turns to be diffusive. So in this case the presence of strong disorder, in the *transition* matrix, only introduces a transient anomalous profile. We say this because asymptotically the mean velocity of the packet $I_1(t\to\infty)$ is just a constant renormalized by the strength of the disorder (i.e., the parameter θ).

Now let us study the second case, i.e., when the strong disorder is present only in the *exchange* matrix, see expressions (29) and (30). Therefore the corresponding $\hat{\eta}(k,u)$ matrix is given by

$$\hat{\eta}(k,u)=\begin{pmatrix} \alpha_1\,\lambda_1(k)\,\phi_1^E(u+\alpha_1) & \psi_{12}^E(u) \\ \psi_{21}^E(u+\alpha_1) & 0 \end{pmatrix}. \tag{41}$$

As before, we assume here that the *exchange* is symmetric $\psi_{12}^E(u)=\psi_{21}^E(u)$, but a nonanalytic function around $u=0$ like in Eq. (28). The current in path B can be calculated using Eq. (41) in Eq. (36) with $l=1$. In this case the current will be characterized by

$$\hat{I}_1(u)=\frac{u\alpha_1(2p_x-1)(\alpha_1+u)^{2\theta}(1+C\,u^\theta)^2 a}{\{\alpha_1 u^\theta+u[(\alpha_1+u)^\theta+u^\theta(1+C\,(\alpha_1+u)^\theta)]\}^2}, \quad \text{for} \quad 0<\theta<1, \tag{42}$$

where we have used the initial condition $\mathbf{P}_0=(1,0)$. This expression gives the behavior of the current into the path B. For example, in this case using the Tauberian theorem we get the asymptotic long-time behavior,

$$I_1(t)\simeq(2p_x-1)\alpha_1^{2\theta-1}\frac{a}{t^{2(1-\theta)}} \quad \text{for} \quad 0<\theta<1, \tag{43}$$

thus, showing an asymptotic vanishing current due to the presence of long-time tail distributions. Physically this behavior is due to the fact that particles that get into stagnant domains, or dead-end volumes, can rarely leave those volumes. These rare events are just characterized by the *exchange* waiting-time distribution $\psi_{12}^E(u)$ (see Appendix A).

The more general case when both *transition* and *exchange* matrices have strong disorder can also be analyzed in the same way by using the corresponding $\hat{\eta}(k,u)$ matrix; work along this line will be presented elsewhere.

B. Application to a Markovian case: The Coats-Smith profile

Here we shall use our method to calculate (in the continuous limit) the Green function of the Coats-Smith equations (1) and (2). From Eq. (35) the matrix Green function of the problem can be found if we known the matrix $\hat{\eta}(k,u)$. As we have remarked before (see Sec. II A 1), using Eq. (23) in the Markovian case $[\psi_1^T(t)=\alpha_1\exp(-\alpha_1 t),\ \psi_{nm}^E(t)=\nu_{nm}\exp(-\nu_{nm}t)]$, and considering the one-dimensional asymptotic Lattice-Fickian operator (38), it is possible to see that the matrix $\hat{\eta}(k,u)$ can be written in the form

$$\hat{\eta}(k,u)=\begin{pmatrix} \dfrac{\alpha_1\left[1-i(1-2p_x)ka-\dfrac{1}{2}(ka)^2\right]}{\alpha_1+u+\nu_{21}} & \dfrac{\nu_{12}}{u+\nu_{12}} \\ \dfrac{\nu_{21}}{\alpha_1+u+\nu_{21}} & 0 \end{pmatrix}. \tag{44}$$

In fact, to solve the Coats-Smith equations (1) and (2) corresponds to studying our MCTRW scheme using Eq. (44) with $\nu_{12}=\nu_{21}=K_c$. The more general case $\nu_{12}\neq\nu_{21}$ can eventually be mapped to the Coats-Smith-Baker [4] model where a fraction $f\propto\nu_{12}$ of the pore volume is available for the flow, while $(1-f)\propto\nu_{21}$ is the stagnant fraction. From now on let us analyze the Coats-Smith model.

The matrix Green function of the corresponding MCTRW, in the lattice representation, is given by

$$\hat{\mathbf{G}}(j,u)=\frac{a}{2\pi}\int_{-\pi/a}^{+\pi/a}\hat{\mathbf{\Phi}}(u)\cdot[\mathbf{1}-\hat{\eta}(k,u)]^{-1}e^{-ikj}\,dk. \tag{45}$$

In the case $a\ll 1$ we can consider the continuous limit $\hat{\mathbf{G}}(j,u)\to\hat{\mathbf{G}}(x,u)\,dx$, therefore Eq. (45) reads

$$\hat{\mathbf{G}}(x,u)\,dx=\frac{dx}{2\pi}\int_{-\infty}^{+\infty}\hat{\mathbf{\Phi}}(u)\cdot[\mathbf{1}-\hat{\eta}(k,u)]^{-1}e^{-ikx}\,dk. \tag{46}$$

Defining the quantities,

$$D_L\equiv\frac{\alpha_1 a^2}{2},\quad V\equiv a(2p_x-1)\alpha_1.$$

The Coats-Smith solution [for a delta initial condition $\delta(x)$] can be read from Eq. (46) if we identify

$$\hat{\mathbf{P}}(k,u)\equiv\hat{\mathbf{G}}(k,u)\cdot\mathbf{P}_0=(\hat{P}_1(k,u),\hat{P}_2(k,u))$$
$$=(\hat{C}_f(k,u),\hat{C}_s(k,u)),$$

where $\mathbf{P}_0=\mathcal{F}_k(C_f(x,0),C_s(x,0))\equiv(C_f(0),C_s(0))$, with $C_f(0)+C_s(0)=1$.

Before taking the inverse Fourier transform (46) we need to calculate the elements of the integrand, $\hat{\boldsymbol{P}}(k,u)\equiv\hat{\mathbf{\Phi}}(u)\cdot[\mathbf{1}-\hat{\boldsymbol{\eta}}(k,u)]^{-1}\cdot\mathbf{P}_0$; therefore using Eqs. (34) and (44) we get the expressions

$$\hat{C}_f(k,u)=\frac{C_s(0)K_c+C_f(0)(K_c+u)}{\mathcal{A}}, \tag{47}$$

$$\hat{C}_s(k,u)=\frac{C_f(0)K_c+C_s(0)(K_c+u+Dk^2-ikV)}{\mathcal{A}}, \tag{48}$$

where $\mathcal{A}=u(2K_c+u)+D_Lk^2(K_c+u)-ikV(K_c+u)$. Note that asymptotically each component $C_f(x,t)$ and $C_s(x,t)$ normalizes to $\frac{1}{2}$; i.e., in the limit $u\to 0$ we get

$$\hat{C}_f(k=0,u)=\hat{C}_s(k=0,u)\sim\frac{1}{2u}.$$

In general, the solution $\hat{C}_f(k,u)$ can be written in the compact form

$$\hat{C}_f(k,u)=\frac{1}{u\mathcal{R}(u)+k^2\mathcal{D}(u)-ik\mathcal{V}(u)}, \tag{49}$$

where

$$\mathcal{R}(u)\equiv\frac{(2K_c+u)}{K_c+C_f(0)u},\quad \mathcal{D}(u)\equiv\frac{D_L(K_c+u)}{K_c+C_f(0)u},$$

$$\mathcal{V}(u)\equiv\frac{V(K_c+u)}{K_c+C_f(0)u}.$$

Therefore the profile $\hat{C}_f(x,u)=\mathcal{F}^{-1}[\hat{C}_f(k,u)]$ is given by [26]

$$\hat{C}_f(x,u)=\frac{1}{2\mathcal{D}(u)}\frac{\exp\left[-|x|\sqrt{\dfrac{u}{D(u)}+\left(\dfrac{V}{2D_L}\right)^2}+x\left(\dfrac{V}{2D_L}\right)\right]}{\sqrt{\dfrac{u}{D(u)}+\left(\dfrac{V}{2D_L}\right)^2}}, \tag{50}$$

where

$$D(u)\equiv\frac{\mathcal{D}(u)}{\mathcal{R}(u)}=\frac{D_L(K_c+u)}{2K_c+u}.$$

From now on we shall use that the physically interesting initial condition is $[C_f(0),C_s(0)]=(1,0)$; therefore we arrive at the expected conclusion that asymptotically, at long time, the Coats-Smith solution behaves likes a Gaussian profile (i.e., solution of a CDE) with coefficients $D_L/2$ and $V/2$,

$$C_f(x,t)\sim\frac{1/2}{\sqrt{4\pi tD_L/2}}\exp\left(-\frac{(x-Vt/2)^2}{4tD_L/2}\right),$$

$$x\in(-\infty,+\infty),\quad t\gg K_c^{-1}.$$

The whole transient behavior can numerically be obtained by calculating the inverse Laplace transform of Eq. (50).

Many other interesting non-Markovian cases, which are in fact related to the problem of disorder, can also be worked out in a similar way from Eq. (35); its analysis will be presented elsewhere.

IV. THE FIRST PASSAGE TIME DISTRIBUTION

The MCTRW approach enables us to estimate the first passage time distribution for the present problem; this distribution is a very important quantity for calculating the exit times of a test particle in complex media. Here it is important

to stress that there exists a fundamental relation between the first passage time distribution (FPTD) to a site j and the propagator to find the particle at this site at time t. This relation expresses that for a Markov process the probability of occurrence of an event at step n is composed of the probability of the *first* occurrence at step n, and of the probability of *first* occurrence at step $n' < n$ times the probability that the event again occurs after the remaining $n-n'$ steps.

Consider a uniform lattice of arbitrary dimensionality and the continuous-time description of a Markov process. Let $F(j,t|0,0)$ be the probability density of *first* arrival at site j at time t, when the particle starts at site $j=0$ and at $t=0$. If the start is not counted as an arrival event, then $F(j=0,t=0|0,0)=0$. Thus the following relation holds [15]:

$$P(j,t|0,0)=\phi(t)\,\delta_{j0}+\int_0^t P(j,t|j,t')F(j,t'|0,0)\,dt', \tag{51}$$

where $\phi(t)$ is the sojourns probability. Using that the lattice is translationally invariant and assuming that the propagator is homogeneous in time, we get

$$P(j,t|0,0)=\phi(t)\,\delta_{j0}+\int_0^t P(0,t-t'|0,0)\,F(j,t'|0,0)\,dt'.$$

This equation can immediately be solved in the Laplace representation,

$$\hat{F}(j,u|0,0)=\frac{\hat{P}(j,u|0,0)-\hat{\phi}(u)\,\delta_{j0}}{\hat{P}(0,u|0,0)}. \tag{52}$$

The important point for considering this result in the context of a stochastic theory with internal states, is the fact that this equation is valid for any Markovian process; thus instead of Eq. (51) we can write the following generalization with internal states [27]:

$$P_{ll'}(j,t|0,0)=\phi_{l'}(t)\,\delta_{j0}\,\delta_{ll'}+\int_0^t P_{ll}(j,t|j,t')\;F_{ll'}(j,t'|0,0)\,dt'. \tag{53}$$

This equation is based on the assumption that different internal states with the same site j, visited by the walker, are counted as distinct events, see our remark in Appendix B. As before, from this equation it is possible to get a solution for $F_{ll'}(j,t'|0,0)$, from the Laplace representation of Eq. (53) we get

$$\hat{P}_{ll}(0,u|0,0)\hat{F}_{ll'}(j,u|0,0)=\hat{P}_{ll'}(j,u|0,0)-\hat{\phi}_{l'}(u)\;\delta_{j0}\,\delta_{ll'}. \tag{54}$$

Now we use that $\hat{P}_{ll'}(j,u|0,0)$ can be written in terms of the inverse Fourier transform of the matrix Green function. Note also that from Eq. (35) we have

$$\hat{P}_{ll'}(k,u|0,0)=\{\hat{\mathbf{\Phi}}(u)\cdot[\mathbf{1}-\hat{\eta}(k,u)]^{-1}\}_{ll'}.$$

So from Eq. (54) ,

$$\hat{F}_{ll'}(j,u|0,0)=\hat{P}_{ll}(j=0,\,u|0,\,0)^{-1}\times[\hat{P}_{ll'}(j,u|0,0)-\hat{\phi}_{l'}(u)\,\delta_{j0}\,\delta_{ll'}],$$

and using that [for example, in two dimensional we have $j\to(j_1,j_2)$; $k\to(k_1,k_2)$ and $a\to(a_1,a_2)$]

$$\hat{P}_{ll'}(j,u|0,0)=\sum_{l''}\hat{\mathbf{\Phi}}(u)_{ll''}\left[\frac{a_1}{2\pi}\frac{a_2}{2\pi}\int_0^{2\pi/a_1}\int_0^{2\pi/a_2}[\mathbf{1}-\hat{\eta}(k,u)]^{-1}\times\exp(-ik\cdot j)\,dk_1dk_2\right]_{l''l'},$$

and, because $\hat{\mathbf{\Phi}}(u)$ is a diagonal matrix we get the final result

$$\hat{F}_{ll'}(j,u|0,\,0)=\hat{\mathbf{\Theta}}_{ll}(j=0,\,u)^{-1}\hat{\mathbf{\Theta}}_{ll'}(j,\,u)-\hat{\mathbf{\Theta}}_{l'l'}(j=0,\,u)^{-1}\,\delta_{j0}, \tag{55}$$

where (in general in n dimensions)

$$\hat{\mathbf{\Theta}}_{ll''}(j,u)=\left[\frac{a_1}{2\pi}\int_0^{2\pi/a_1}\cdots\frac{a_n}{2\pi}\int_0^{2\pi/a_n}[\mathbf{1}-\hat{\eta}(k,u)]^{-1}\times\exp(-ik\cdot j)dk_1\cdots dk_n\right]_{ll''}.$$

Equation (55) gives the desired result, i.e., the FPTD (in its Laplace representation) from the origin $j=0$ with internal state l' at time $t=0$, to site j with internal state l at time t; therefore the problem has been reduced to the calculation of an inverse Fourier-Laplace transform.

Now going back to our original problem, we have to consider that each internal state represents a possible path l. Nevertheless, a new difficulty appears in our approach, and it is due to the fact that our generalized MCTRW (a possible generalized Coats-Smith model) could also be a non-Markovian process due to the memory effects introduced by the disorder average. Then we only can use Eq. (55) as an approximation. Unfortunately this, of course, is not a perturbative approximation; but our result gives a plausible approach to the problem of solving the FPTD for a non-Markovian process, which in fact is a nontrivial problem [18]. Indeed, in a future paper we will analyze this distribution in the context of a characterization of the concentration profile in a disordered medium with multiple transport paths [28].

A. The first passage time distribution for the Coats-Smith model

Here we shall use our approach to calculate the *first passage time distribution* associated with the Coats-Smith equations (1) and (2), i.e., a Markovian example. In this case the probability distribution to reach the position $x=L>0$ for the

first time, when the particle starts its walk from position $x=0$ at time $t_0=0$, is given by the first passage time distribution (in its Laplace representation), $\hat{F}_L(u) \equiv \hat{F}_{11}(L,u|0,0)$. Therefore from Eq. (55) we have

$$\hat{F}_L(u)=\frac{\hat{\mathbf{\Theta}}_{11}(x=L,\,u)}{\hat{\mathbf{\Theta}}_{11}(x=0,\,u)}. \tag{56}$$

Using the results of Sec. III B [with the initial condition $C_f(0)=1$] it is simple to see, from Eq. (50), that

$$\hat{F}_L(u)=\frac{\hat{C}_f(L,\,u)}{\hat{C}_f(0,\,u)} =\exp\left[-L\sqrt{\frac{u}{D(u)}+\left(\frac{V}{2D_L}\right)^2}+L\left(\frac{V}{2D_L}\right)\right], \tag{57}$$

where

$$D(u)=\frac{D_L(K_c+u)}{2K_c+u}.$$

Formula (57) is an exact result; from this expression it is simple to see that after a time of the order of K_c^{-1}, the first passage time distribution can be approximated by using

$$\hat{F}_L(u)\simeq\exp\left[-L\sqrt{\frac{2u}{D_L}+\left(\frac{V}{2D_L}\right)^2}+L\left(\frac{V}{2D_L}\right)\right]. \tag{58}$$

This expression can immediately be transformed to its time representation; then taking the inverse Laplace transform of Eq. (58) we get the FPTD [29],

$$F_L(t)\simeq\exp\left[\frac{V}{2D_L}\left(L-\frac{Vt}{4}\right)\right]\frac{L\,t^{-3/2}}{\sqrt{2\pi D_L}}\exp\left[\frac{-L^2}{2D_L t}\right], \quad t\gg K_c^{-1}. \tag{59}$$

Remark. As we have mentioned before, there is no *simple* perturbative approximation to calculate $F_L(t)$ for a non-Markovian process; nevertheless, our result (55) gives a plausible method to tackle the problem of calculating the FPTD. Indeed, this is a possible approach to analyze secondary oil recovery in a disordered medium, work along this line will be reported elsewhere [28].

1. Scaling results

From the result (57) we realize that introducing the change of variables,

$$t=\tau\left(\frac{D_L}{V^2}\right), \quad x=\chi\left(\frac{D_L}{V}\right),$$

the FPDT (in its Laplace representation) can be written in a *simple* dimensionless form,

$$\hat{F}_{\mathsf{L}}(U)=\exp\left(-\mathsf{L}\sqrt{\frac{U(2\varkappa_c+U)}{(\varkappa_c+U)}+\frac{1}{4}}+\frac{\mathsf{L}}{2}\right) \quad \text{where} \quad U=u\left(\frac{V^2}{D_L}\right)^{-1}, \quad \mathsf{L}>0, \tag{60}$$

and L is a dimensionless distance. Therefore after a transient time of the order of

$$\varkappa_c^{-1}\equiv(K_c D_L/V^2)^{-1},$$

the FPTD of the Coats-Smith process can be approximated by the universal function

$$F_{\mathsf{L}}(\tau)\sim F_{\mathrm{Gauss}}(\tau,\mathsf{L})=\frac{\mathsf{L}\tau^{-3/2}}{\sqrt{2\pi}}\exp\left[\frac{\mathsf{L}}{2}-\frac{\tau}{8}-\frac{\mathsf{L}^2}{2\tau}\right], \quad \tau\gg\varkappa_c^{-1}. \tag{61}$$

From this expression it is simple to see that the maximum of the FPTD, $F_{\mathrm{Gauss}}(\tau,\mathsf{L})$, is located at

$$\tau_M=-6+2\sqrt{9+\mathsf{L}^2}.$$

Thus, if $\tau_M\gg\varkappa_c^{-1}$, it means that the transient in the Coats-Smith profile is not important because it is very early than the time scale where the maximum of the CDE profile is located; then, in order to study the hydrodynamics dispersion it is suitable to represent the whole $F_{\mathsf{L}}(\tau)$ by the Gaussian approximation $F_{\mathrm{Gauss}}(\tau,\mathsf{L})$. Nevertheless, if $\tau_M\lesssim\varkappa_c^{-1}$ the transient in the Coats-Smith profile is very important; this fact can also be understood in terms of a system-size analysis. From the condition $\tau_M\lesssim\varkappa_c^{-1}$, it follows that

$$\mathsf{L}\lesssim\sqrt{\left(\frac{\varkappa_c^{-1}+6}{2}\right)^2-9}\equiv\mathsf{L}_c, \tag{62}$$

where L_c is a critical value that characterizes the importance of the Coats-Smith transient. Thus for a given value of the (dimensionless) parameter $\varkappa_c^{-1}$, the FPTD of the system will show a finite-size transient behavior only if $\mathsf{L}\lesssim\mathsf{L}_c$. It is trivial to realize that if $\varkappa_c\gg1$ there will not be anomalous transient hydrodynamics dispersion for any size scale $\mathsf{L}>0$, this fact is in agreement with an Heuristic analysis that can be done by direct inspection in the Coats-Smith equation.

Before ending this section let us remark that the characterization of the critical distance L_c is a result that helps to solve the controversial question about the origin of the anomalous transient and finite-size effects.

In Figs. 1(a, b) we have plotted for several values of $\varkappa_c=(0.1,1,10)$ and $\mathsf{L}=(1,5)$, the CDE approximation (61) against the exact result obtained numerically [30] by calculating the inverse Laplace transform of Eq. (60). On the other hand, form (62) and for the mentioned values of $\varkappa_c$ we get different critical values L_c, thus, for example,

$$\varkappa_c=0.1\Rightarrow\mathsf{L}_c=7.4162,$$

$$\varkappa_c=1\Rightarrow\mathsf{L}_c=1.8027,$$

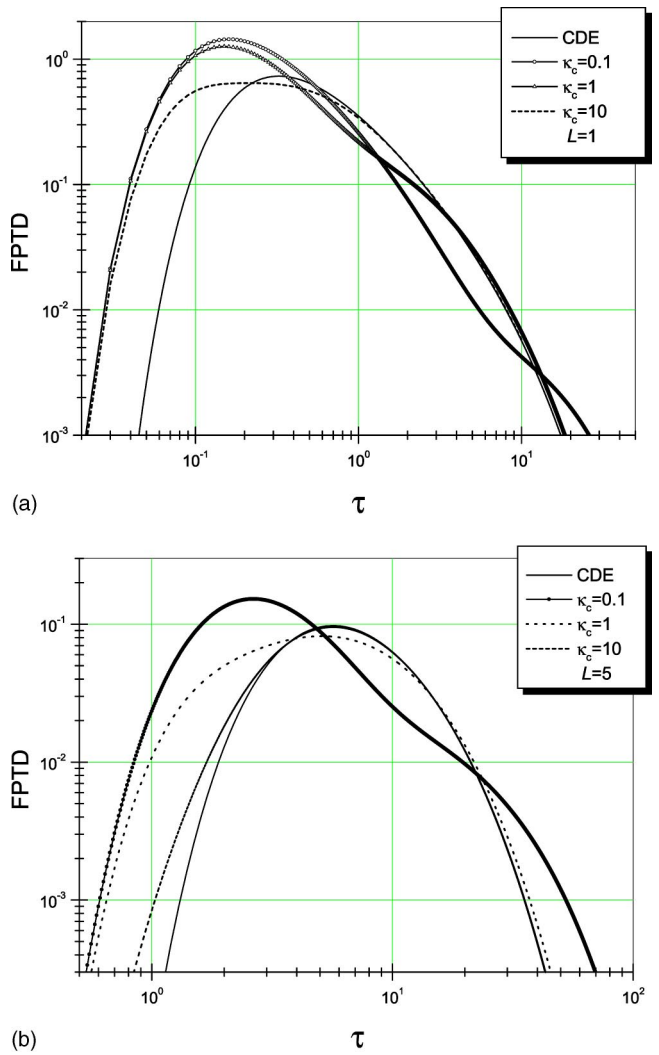

FIG. 1. (a) Log-log plot for the FPTD of the Coats-Smith process [obtained form Laplace inversion of Eq. (60)] as a function of τ (dimensionless time) for $\mathsf{L}=1$ (dimensionless distance) for several values of $\varkappa_c(=0.1,1,10)$ against the FPTD associated with the CDE process (the Gaussian approximation (61)). Log-log plot for the FPTD of the Coats-Smith process as a function of τ for $\mathsf{L}=5$ for several values of $\varkappa(=0.1,1,10)$ against the FPTD associated with the CDE process; using the same dimensionless units as in (a).

$$\varkappa_c = 10 \Rightarrow \mathsf{L}_c = 0.55.$$

From Figs. 1(a, b) it is simple to check our prediction that for $\mathsf{L} \lesssim \mathsf{L}_c$ the system-size analysis is very relevant.

Remark. Note that the presence of weak disorder reduces the dispersion coefficient [i.e., in an effective medium approximation $D_L = \frac{1}{2}(d/dt)[\langle x^2\rangle - \langle x\rangle^2] \to D_{eff} \propto \langle 1/w\rangle^{-1}$, see for example, Appendix A], then $\varkappa_c = K_c D_L / V^2$ will be reduced too, and this fact will lead to an increase of the critical distance L_c, which ultimately will enhance the finite-size effects and consequently the transient anomalous dispersion in the Coats-Smith approach.

It would be very important to have similar conclusions concerning the scaling of the FPTD in the presence of strong disorder; work along this line is in progress.

V. DISCUSSION

Many models of disorder can be studied from our mesoscopic point of view, and such analysis could help to understand more complex systems (concerning hydrodynamic dispersion in disordered media) that cannot be described by a CDE or a Coats-Smith model. In particular, if in addition to the heterogeneity there are multiple families of transport paths, which could appear due to fractures in porous rocks, this situation, in principle, can also be analyzed using the present approach. Therefore, for example, the first passage time distribution of the test particle can be estimated; or the transient and the long-time response to the injection of a pulse can be calculated, etc. In particular, we have confined our attention to models of *transition disorder* and *exchange disorder*. Transition disorder corresponds to randomness in the shapes and sizes of the microscopic elements of the transport paths; and exchange disorder corresponds to an asymmetry in the exchange between the different paths [13,14]. Just in order to unify the nomenclature with previous literature—in the subject of disordered transport with multiple paths—let us now make a summary about the classification of *transition* and *exchange* disorder. Consider a two-path system, then the structure of the *supermatrix* Ψ is the one that appears in Eq. (4), so it is possible to realize that our matrix B_{ij} is related to the matrix $\mathbf{W}_{ij}^{11}$ of Ref. [14], and so A_{ij} is related to the matrix $\mathbf{W}_{ij}^{22}$. On the other hand, the probability $\psi_j^{BA}(t)\,dt$ is related to probability rate $\mathbf{E}_j^{12}$ at site j, and so $\psi_j^{AB}(t)\,dt$ is related to $\mathbf{E}_j^{21}$. Thus after introducing the Hartree approximation, Eqs. (5) and (6), etc., it is clear that the MCTRW approach induces not only memory, but also additional coupling between the different paths as can be seen from the structure of Eq. (12). As a matter of fact from this structure it is simple to see that the *exchange* transitions are only associated *without changes of site*, this result of course was expected from the proposed structure (4).

There are also other remarks concerning our approach.

(a) The present formulation allows us to work out transition disorder *with* bias; as can be seen, for example, from Eq. (21). This is something that was excluded from the approach of Ref. [14] (because $\mathbf{W}_{ij} = \mathbf{W}_{ji}$), although the presence of a macroscopic flow velocity is a fundamental ingredient in the study of hydrodynamic dispersion. In fact, to solve an EMA with bias, without internal states, is a nontrivial problem; see, for example, Ref. [24].

(b) The calculation of the first passage time distribution can be done, at least in some approximation, thus the finite-size effects can be studied. This calculation is something that appears more subtle in the context of EMA (even for the case without internal states); see, for example, Ref. [31].

(c) Non-Fickiang operators can be introduced in our approach to characterize some special transport mechanism in one of the paths; for example, transport in the fracture network of a reservoir is much faster than that in the pores. Thus using that the transport in a random network of fracture can be described in terms of a space-time coupled function, $\psi_l^T(k,u)$, see Ref. [25], we can introduce the occurrence of stagnant volumes in the description by considering a second

alternative path like the one we have mentioned all along the paper.

(d) Another alternative is to consider the presence of random advection in the description of the problem. For example, if the mean velocity of the flow V is replaced by a random vector field $V(r,t)$, the CTRW theory can also be used to tackle this problem [32]; this situation is very important in the geological analysis of stratified disordered media [33]. Then we can use the present MCTRW approximation to consider this type of disorder and in addition with stagnant domains (multiple paths).

Here it is important to remark that even when the MCTRW approach looks very powerful, the reader should not forget that the CTRW theory does not give the correct anomalous exponent of the frequency-dependent diffusion coefficient; neither can it describe a percolation binary mixture (see, for example, Refs. [34,35]). Thus the present MCTRW approach should be considered as a sort of parametric description for the mesoscopic problem, but with the possibility to obtain an analytic formula for the first passage time distribution. Therefore our approximation allows us to calculate not only the long-time behavior but also the transient of complex systems like the one we have reported along this paper. As a matter of fact in a future work [28], we are going to analyze secondary oil recovery, by doing nonlinear least-square fits from our analytic solution in the Laplace representation, see Eq. (55).

A. Concerning the different waiting time functions

Suppose that we want to study an heterogeneous system where the stagnation times are characterized by a typical *distribution*. The crudest approximation is to assume which there is a *characteristic time*, given by a mean value of a certain random variable w, which characterizes the ''symmetric transition rate'' to get *in* or *out* of the stagnant volumes. This approximation leads to the conclusion that $\hat{\psi}^E(u)$ is given by an exponential waiting-time function with $\langle 1/w\rangle^{-1}=K_c$, see Eq. (A8). By doing this we just reobtain the Coats-Smith phenomenological model (1). So if we want to improve this approximation we could use an expansion like Eq. (A7) to calculate each of the waiting-time functions $\hat{\psi}^E_{21}(u)$ and $\hat{\psi}^E_{12}(u)$ that characterize the *exchange disorder*. Now suppose that the system presents long waiting times that characterize the different stagnation times of the medium, due, for example, to the occurrence of a broad distribution in the porosity of the system (noninterconnected pores). In this case (as was shown in Appendix A) the function $\hat{\psi}^E_{ll'}(u)$ is not analytic around $u\sim 0$. Thus, for example, $\psi^E(t)$ is of the form (A4), and so its Laplace transform can be parametrized by the expression (28).

Consider now the *transition disorder*, so, for example, we can study the characterization of the macroscopic kinetic coefficient D_L that appear in Eq. (1). On the other hand, in the phenomenological approach the mean flow velocity is V, then in order to calculate the *average* over disorder of $(d/dt)j(t)$, we can use the Green function given in Sec. III. For example, suppose that there is only one transport path (the path B) and the presence of *transition* weak disorder is introduced by using the waiting time function, $\hat{\psi}^T_1(u)=(1+\tau u)^{-b}$ with $\{b\geqslant 1,\tau>0\}$ (this function is associated with a gamma distribution for the waiting times of the RW into the transport channel; if $b=1$ there is no *disorder*). Assuming, as is usual in the CTRW theory, that all the lattice sites are topologically equivalent, we can adopt a two-dimensional hopping structure function as the one given in Eq. (22), then it is simple to see that $(d/dt)\langle\overline{j(t)}\rangle\propto V/b$ with $V\propto(2p_y+2p_x-1)a/\tau$ in the continuous limit.

B. Summary of the present approach

The finite-size effects can be studied, see, for example, Eq. (62). The present approach gives us the possibility to study the occurrence of different scaling regimes and asymptotic universal forms—for the problem of finite-size anomalous hydrodynamic dispersion—as we have done in the Markovian approximation in Sec. IV A 1; i.e., from Eq. (55) a formula for the FPDT generalizing Eq, (57) can be written considering disorder in the interconnected and noninterconnected pores (backbone and dead-end domains).

Our approximation allows us to introduce non-Fickian operators (with or without bias), and consider models where *exchange* and *transition* disorder are present simultaneously; this is something that in the context of the EMA with multiple paths has not been treated [14].

We would like to emphasize that an analysis with different boundary conditions can also be worked out because we know the matrix Green function (with multiple paths), see Eq. (35).

Before ending this section let me comment about a very interesting paper concerning *noninterconnected pores* (porosity and permeability) written by de Gennes [36] (a simpler description was also given in Ref. [37]). de Gennes studied stagnation effects in the hydrodynamic dispersion in unsaturated porous media, making a connection with the topology of the infinite cluster in a percolation problem. He was able to predict the behavior of the dispersion coefficient D_L as a function of the macroscopic flow velocity, the percolation correlation length, and the diffusion constant in the absence of flow. Here I should tell that *the* de Gennes approach, the EMA with multiple paths, and the MCTRW approximation complement each other to tackle the still fascinating subject of anomalous hydrodynamic dispersion in heterogenous media.

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APPENDIX A: THE WAITING-TIME FUNCTION AND THE MODELS OF DISORDER

Depending on the analyticity (around $u\sim 0$) of the waiting-time function $\hat{\psi}(u)$ it is possible to characterize dif-

ferent types of disorder. In the context of the CTRW there exists a clear relation between a model of disorder and the waiting-time function, which is given by [22]

$$\psi(s-s',t)=\left\langle W_{s,s'}\exp\left(-t\sum_{s} W_{s,s'}\right)\right\rangle_{\text{Disorder}}. \quad \text{(A1)}$$

In the present paper we are dealing with a family of multiple paths, so we have introduced internal states in the description of the process, that is why here we are interested in a MCTRW; thus we have to calculate an average as in Eq. (5) or Eq. (6).

Let us consider the *exchange* probabilities, i.e., for example, assume that there are only two possible paths, then for a given realization of the disorder the waiting time for the *exchange* from path B to A is

$$\psi_j^{AB}(t)=\mathcal{W}^{AB}(j)\exp[-\mathcal{W}^{AB}(j)\,t],$$

where, in principle, $\mathcal{W}^{AB}(j)$ is an arbitrary probability rate that indeed depends on the site j. The fundamental *ansatz* in order to be able to calculate the average over the disorder is that $\mathcal{W}^{AB}(j)$ is a random variable equally distributed over the sites of the lattice. Then it follows that

$$\begin{aligned}\langle \mathcal{W}^{AB}(j)\exp[-\mathcal{W}^{AB}(j)\,t]\rangle_{\text{Disorder}} &= \int w\exp(-w\,t)\,\mathcal{P}(w)\,dw \\ &\equiv \langle w\exp(-w\,t)\rangle. \end{aligned} \quad \text{(A2)}$$

It is now clear that depending on the nature of the probability density $\mathcal{P}(w)$, different waiting-time functions will arise. Consider, for example, a model of strong disorder (i.e., there is a chance to get $w=0$ with a finite probability),

$$\mathcal{P}(w)=\begin{cases}\dfrac{\theta}{w_0}(w/w_0)^{\theta-1}, & 0\leqslant w\leqslant w_0,\quad \theta\in(0,1)\\ 0, & w>w_0.\end{cases} \quad \text{(A3)}$$

Then from Eq. (2) we get

$$\psi_{21}^{E}(t)=\frac{\theta w_0}{\tilde{t}^{\theta+1}}\gamma(\theta+1,\tilde{t}),\quad \theta\in(0,1)\quad \text{with}\quad \tilde{t}=w_0 t. \quad \text{(A4)}$$

Here $\gamma(\theta+1,\tilde{t})$ is the gamma incomplete function, thus for $\tilde{t}\to\infty$ we can use $\gamma(\theta+1,\tilde{t})\to\Gamma(\theta+1)$, and from this we get an asymptotic expression (for long times) for the waiting-time function

$$\psi_{21}^{E}(t)\sim\frac{\theta\Gamma(\theta+1)}{w_0^{\theta}t^{\theta+1}},\quad \theta\in(0,1), t\to\infty. \quad \text{(A5)}$$

It is simple to see that the Laplace transform of this asymptotic expression is (using the Tauberian theorem around $u\sim 0$)

$$\hat{\psi}_{21}^{E}(u)\sim 1-Cu^{\theta},\quad u\to 0,\theta\in(0,1),C=\text{const}. \quad \text{(A6)}$$

From this expression we see that for $\theta\in(0,1)$, the function $\hat{\psi}_{21}^{E}(u)$ is not analytic around $u=0$.

If instead of Eq. (B3) we use a probability distribution such that $\lim_{w\to 0}\mathcal{P}(w)\to 0$ (weak disorder), the average (B2) may lead to a waiting time which can be an analytic function around $u=0$. Thus, for example, the quantity $-d\hat{\psi}_{21}^{E}(u)/du|_{u=0}=\int_0^\infty \tau\psi_{21}^{E}(\tau)\,d\tau=\langle t\rangle$ is well defined, and it is in fact the mean waiting time. This result shows that weak disorder can lead to memory functions (when the waiting time is not exponential) but with a well-defined mean waiting time [20–22]. Alternatively, this effective waiting-time function can be calculated using the fact that $\hat{\psi}(u)=1-u\hat{\phi}(u)$, where $\hat{\phi}(u)=\langle 1/(u+w)\rangle$. Then, if the quantities $\langle(1/w)^m\rangle$, $\forall m=1,2,\ldots$ are well defined, we can write the series expansion

$$\hat{\psi}(u)=1-u\hat{\phi}(u)=1-\left\langle\frac{u}{u+w}\right\rangle=\sum_{m=0}^{\infty}(-u)^m\left\langle\left(\frac{1}{w}\right)^m\right\rangle. \quad \text{(A7)}$$

Thus, in the presence of weak disorder we can write asymptotically

$$\lim_{u\to 0}\hat{\psi}(u)\simeq 1-u\left\langle\frac{1}{w}\right\rangle\simeq\left(1+\left\langle\frac{1}{w}\right\rangle u\right)^{-1},$$

which means that at long time and if the disorder is weak, we can approximate the waiting time by an effective exponential function

$$\psi(t)\approx\left\langle\frac{1}{w}\right\rangle^{-1}\exp\left(-\left\langle\frac{1}{w}\right\rangle^{-1}t\right). \quad \text{(A8)}$$

This result, in the context of the CTRW, corresponds to the conclusion that weak disorder renormalizes the kinetic coefficients.

APPENDIX B: THE FIRST PASSAGE TIME DISTRIBUTION

Depending on the meaning of the internal states l an alternative definition for the FPTD can be introduced. Thus, here we are going to present a different point of view to define the FPTD in the presence of internal states. If the lattice itself is homogeneous [27] but the walker can be in different internal states *at a given site* (i.e., spin $\frac{1}{2}$ or $\frac{-1}{2}$), so (j,l'') and (j,l) represent different states at the same site, then Eq. (53) should be replaced by

$$P_{ll'}(j,t|0,0)=\phi_{l'}(t)\ \delta_{j0}\delta_{ll'} + \int_0^t \sum_{l''} P_{ll''}(j,t|j,t')F_{l''l'}(j,t'|0,0)dt'. \tag{B1}$$

As before, from this equation it is possible to get a solution for $F_{l''l'}(j,t'|0,0)$. From the Laplace representation of Eq. (1) we get

$$\sum_{l''} \hat{P}_{ll''}(0,u|0,0)\hat{F}_{l''l'}(j,u|0,0) = \hat{P}_{ll'}(j,u|0,0)-\hat{\phi}_{l'}(u)\ \delta_{j0}\ \delta_{ll'}. \tag{B2}$$

Now we can use that $\hat{P}_{ll''}(j,u|0,0)$ can be written in terms of the inverse Fourier transform of the matrix Green function. Therefore from Eq. (35) we have in n dimensions,

$$\hat{P}_{ll''}(j,u|0,0)=\frac{a_1}{2\pi}\int_0^{2\pi/a_1}\cdots\frac{a_n}{2\pi}\int_0^{2\pi/a_n}[\hat{\mathbf{\Phi}}(u)\cdot\hat{\mathbf{\Theta}}(k,u)]_{ll''}\exp(-ik\cdot j)\ dk_1\ \ldots\ dk_n. \tag{B3}$$

From the definition $\hat{\mathbf{\Theta}}(k,u)\equiv[\mathbf{1}-\hat{\eta}(k,u)]^{-1}$, and using the inverse matrix of Eq. (3) in Eq. (2) we get the final result

$$\hat{F}(j,u|0,0)=\hat{\mathbf{\Theta}}(j=0,u)^{-1}\cdot\hat{\mathbf{\Theta}}(j,u)-\hat{\mathbf{\Theta}}(j=0,u)^{-1}\delta_{j0}\ \delta_{ll'}. \tag{B4}$$

Here $\hat{F}(j,u|0,0)$ indicates a matrix with the elements $\hat{F}_{ll'}(j,u|0,0)$, and

$$\hat{\mathbf{\Theta}}(j,u)=\frac{a_1}{2\pi}\int_0^{2\pi/a_1}\cdots\frac{a_n}{2\pi}\int_0^{2\pi/a_n}[\mathbf{1}-\hat{\eta}(k,u)]^{-1} \times\exp(-ik\cdot j)\ dk_1\ \ldots\ dk_n.$$

Equation (B4) gives the desired result (in its Laplace representation), i.e., the FPTD from the origin $j=0$ with internal state l' at time $t=0$, to site j with internal state l at time t; counting the different events (mutually exclusive) to give the possibilities to reach the state (j,l) passing through all the states (j,l''). Compare the subtle difference with the result given in Eq. (55). For example, here the return to the origin is expressed by the formula

$$\hat{F}_{ll}(j=0,u|0,0)=1-[\hat{\mathbf{\Theta}}(j=0,\ u)^{-1}]_{ll}.$$

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