Is There a Representative Elementary Volume for Anomalous Dispersion?

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Abstract The concept of the representative elementary volume (REV) is often associated with the notion of hydrodynamic dispersion and Fickian transport. However, it has been frequently observed experimentally and in numerical pore scale simulations that transport is non-Fickian and cannot be characterized by hydrodynamic dispersion. Does this mean that the concept of the REV is invalid? We investigate this question by a comparative analysis of the advective mechanisms of Fickian and non-Fickian dispersion and their representation in large scale transport models. Specifically, we focus on the microscopic foundations for the modeling of pore scale fluctuations of Lagrangian velocity in terms of Brownian dynamics (hydrodynamic dispersion) and in terms of continuous time random walks, which account for non-Fickian transport through broad distributions of advection times. We find that both approaches require the existence of an REV that, however, is defined in terms of the representativeness of Eulerian flow properties. This is in contrast to classical definitions in terms of medium properties such as porosity, for example.

Keywords Representative elementary volume · upscaling · anomalous dispersion · continuous time random walks · velocity statistics

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1 Introduction

The notion of a representative elementary volume (REV) lies at the heart of macroscopic (continuum) descriptions for systems that exhibit small scale structural disorder (caused by the mixture of void and solid phases that forms the porous medium), feature which is usually referred to as material heterogeneity. In the frame of continuum approaches, the REV is associated to a point of the continuous field where average properties, that are supposed to denote the effective properties of the material, are allocated. For instance permeability, from which the average fluid velocity is derived, and hydrodynamic dispersion are critical properties for modeling steady state flow and solute transport, respectively. The REV corresponds to the (minimum) volume required to evaluate the effective properties of a heterogeneous material or, in other words, the minimum volume above which the properties are stationary. This is illustrated in Figure 1 for the ratio of void to bulk volume, i.e. the porosity, where the REV size is determined from the constant limit value of ϕ_ℓ:

$$\phi_\ell = \frac{1}{V_\ell} \int_{\Omega_\ell} d\mathbf{x} \mathbb{I}(\mathbf{x} \in \Omega_f), \tag{1}$$

where Ω_f and Ω_ℓ denote the fluid domain and bulk domain of volume ℓ, V_ℓ respectively and $\mathbb{I}(\cdot)$ is the indicator function, which is equal to 1 if its argument is true and 0 otherwise. The length scale ℓ at which ϕ_ℓ stabilizes defines the REV scale.

Accordingly, the REV is clearly definable for two extreme cases: 1) unit volume in a periodic microstructure, and 2) a volume containing a large set of micro-scale structures displaying homogeneous and ergodic properties. The existence of the REV relies on the existence of scale separation of spatial medium fluctuations. An REV cannot be defined for continuously hierarchized heterogeneous media such as fractal materials. The REV is typically determined from applying this concept to the material microstructure and specifically to its simplest quantitative notion, which is its porosity (as illustrated in Figure 1). Porosity is easily measurable at laboratory scale and can also be determined at pore-scale by using imaging methods such as computed microtomography which allows characterizing the micro-structures over volumes that are typically larger than the REV. Since the REV can be well-defined for porosity, it is generally assumed that this definition also implies the existence of transport relevant parameters such as the specific discharge and the hydrodynamics dispersion coefficients. The former represents the mean pore velocity, the latter quantifies its fluctuations. The values of these parameters are considered to be well-defined and constant on the REV scale. Note that assuming the specific discharge constant within the REV implies that the product of permeability and the pressure gradient is constant. This stems from the Darcy equation, which states that

$$q = -\frac{k}{\mu} \frac{dP(x_1)}{dx_1}, \tag{2}$$

where k is permeability, $P(x_1)$ is pressure and μ dynamic viscosity. The assumption that the REVs for the porosity and the specific discharge are the same is not evident. The assumption that the REVs for the porosity and for the hydrodynamics dispersion

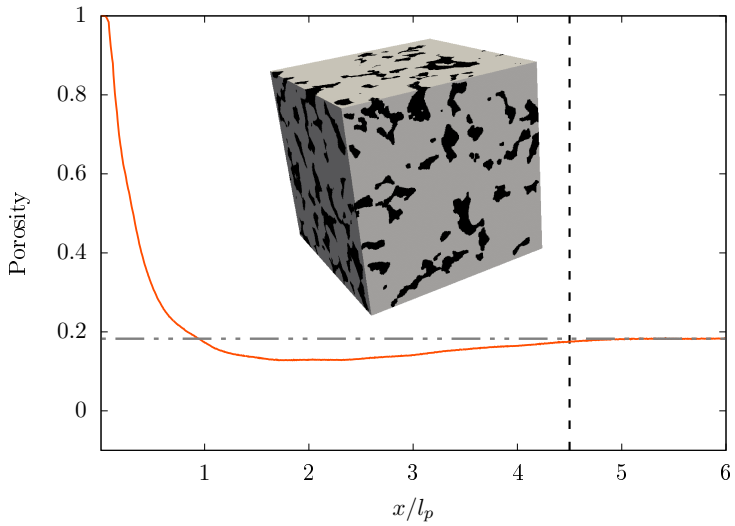

Fig. 1 Porosity measured in a cube of increasing side length cube (x-axis) centered in the middle of the Berea sandstone sample studied in Section 2. The side length of the full sample is $6\ell_p$ and its porosity is 0.182 (gray dashed line). $\ell_p \approx 1,5 \cdot 10^{-4}$ m denotes the average pore length.

coefficients are similar is even less evident because the later encompasses the impact of pore-scale velocity fluctuations. Yet, if this assumption holds, average solute transport can be described by the advection-dispersion equation (ADE) (Bear, 1972)

$$\phi \frac{\partial c(x_1,t)}{\partial t} + q \frac{\partial c(x_1,t)}{\partial x_1} - \mathscr{D} \frac{\partial^2 c(x_1,t)}{\partial x_1^2} = 0. \tag{3}$$

This approach described Darcy-scale transport in terms of porosity ϕ, specific discharge q and the hydrodynamic dispersion coefficient $\mathscr{D}$.

Experimental (Moroni and Cushman, 2001; Cortis and Berkowitz, 2004; Holzner et al, 2015; Morales et al, 2017) and numerical (Bijeljic and Blunt, 2006a; Bijeljic et al, 2011; Liu and Kitanidis, 2012; De Anna et al, 2013; Kang et al, 2014; Meyer and Bijeljic, 2016; Puyguiraud et al, 2019a; Dentz et al, 2018) pore scale studies observed deviations from predictions based on the ADE (3). This includes tailing in solute breakthrough curves, non-linear growth of dispersion and non-Gaussian particle distributions and propagators. Such behaviors are usually modeled based on non-local transport approaches such as multirate mass transfer and continuous time random walks (Berkowitz et al, 2006; Noetinger et al, 2016) as well as fractional dynamics (Cushman and Moroni, 2001).

In this paper, we investigate the notion of REV for non-Fickian dispersion. We scrutinize the assumptions underlying modeling approaches for Fickian and non-Fickian dispersion and the relation with the REV concept. In Section 2.2.1 we discuss the bases of the ADE framework and we include a critical revision of its limitations. In Section 2.2.2 we discuss the framework of continuous time random walk models

and investigate what underlying assumptions they are relying on. This leads us to define, in Section 2.3 the Eulerian REV for anomalous transport and to illustrate its evaluation from computations performed using a digitized volume of a real rock sample in Section 2.5. The implications of such an REV definition for continuum scale modeling of Fickian and non-Fickian transport are discussed in section 3.

2 Dispersion upscaling and the representative elementary volume

In this section, we consider the assumptions that support the description of solute dispersion by advection-dispersion models and continuous time random walks. From these considerations we propose the definition of an REV in terms of the Eulerian flow statistics, and discuss conditions on the Lagrangian velocity statistics.

2.1 Pore scale flow and transport

Pore scale flow is described here by the Stokes equation

$$\nabla^2 \mathbf{u}(\mathbf{x}) = -\frac{\nabla p(\mathbf{x})}{\mu}, \tag{4}$$

together with the incompressibility assumption $\nabla \cdot \mathbf{u}(\mathbf{x}) = 0$. The mean pressure gradient is aligned with the 1-direction of the coordinate system. We consider purely advective transport that is described by the kinematic equation

$$\frac{d\mathbf{x}(t,\mathbf{a})}{dt} = \mathbf{v}(t,\mathbf{a}), \tag{5}$$

where $\mathbf{x}(t=0,\mathbf{a}) = \mathbf{a}$ and $\mathbf{v}(t,\mathbf{a}) = \mathbf{u}[\mathbf{x}(t,\mathbf{a})]$ is the Lagrangian velocity. We disregard diffusion and focus on the advective particle motion along the streamlines as the sole mechanism by which the velocity field is sampled. The impact of diffusion on the results presented in the following, are discussed in Section 3. Equation (5) can be transformed into streamline coordinates $t \to s$, with

$$\frac{ds(t)}{dt} = v(t), \tag{6}$$

where $v(t) = |\mathbf{v}(t)|$. This gives the equivalent system of equations

$$\frac{d\mathbf{x}(s,\mathbf{a})}{ds} = \frac{\mathbf{v}(s,\mathbf{a})}{v(s,\mathbf{a})}, \qquad \frac{dt(s,\mathbf{a})}{ds} = \frac{1}{v(s,\mathbf{a})}. \tag{7}$$

2.2 Dispersion upscaling

We consider the conditions under which pore-scale velocity fluctuations can be quantified by the concept of hydrodynamic dispersion and how this relates to the notion of an REV. Then, we discuss the same issues for continuous-time random walk models to upscale anomalous dispersion.

2.2.1 Fickian dispersion

In order to identify the basic assumption underlying the ADE formulation of Darcy-scale transport, we consider the Langevin equation (Gardiner, 2010) that is equivalent to the ADE (3),

$$\frac{dx(t)}{dt} = \bar{v}_1 + v_1'(t), \tag{8}$$

where we decomposed the particle velocity $v_1(t)$ into its mean $\bar{v}_1$ and fluctuation $v_1'(t)$. The mean pore velocity is $\bar{v}_1 = q/\phi$. The velocity fluctuation $v_1'(t)$ is represented by a stationary Gaussian random process characterized by 0 mean and the covariance function

$$\langle v_1'(t) v_1'(t') \rangle = 2\mathscr{D}\delta(t-t'), \tag{9}$$

where $\mathscr{D}$ is the hydrodynamic dispersion coefficient and $\delta(t)$ is the Dirac Delta. The angular brackets denote the average over the ensemble of the noise realizations. With these properties of the velocity fluctuations, Equation (8) describes Brownian dynamics.

The representation of the velocity fluctuations as a δ-correlated Gaussian process is based on several conditions. First, the velocity process needs to be stationary and ergodic. This means that its mean and variance depend only on the time lag and not on the absolute time. Second, velocity fluctuations decay exponentially fast on a characteristic correlation time scale τ_c. Furthermore, based on the assumption that the velocity distribution has finite variance, the displacement distribution, which is the sum of random velocity increments, converges towards a Gaussian distribution as time increases. This is a consequence of the central limit theorem (Gardiner, 2010) and warrants the modeling of the statistics of $v_1'(t)$ as Gaussian. The correlation model (9) is valid at observation times that are much larger than the correlation scale τ_c, which can be related to the advection time over a characteristic length scale ℓ_c,

$$\tau_c = \frac{\ell_c}{\bar{v}_1}. \tag{10}$$

This implies that for time $t \gg \tau_c$, particles must have access to the full spectrum of velocity variability. The Langevin equation (8), which is valid at $t \gg \tau_c$, thus implies that at each random walk step, particles can sample the full spectrum of random velocities. Particles become statistically equal on the time scale τ_c. This temporal notion can be related to a spatial REV scale through the length scale ℓ_c that is assumed to mark the correlation time together with the mean velocity $\bar{v}_1$. Thus, the REV scale is supposed to contain a representative set of flow velocities that particles can sample with equal probability. This is discussed further in Section 2.3.

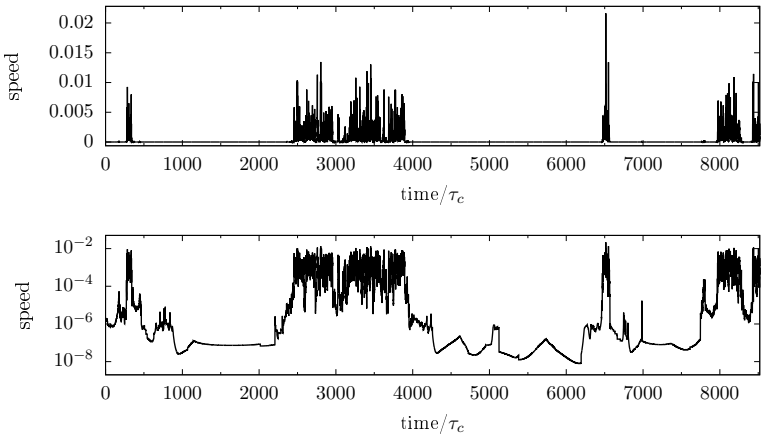

Fig. 2 Time series of velocity magnitudes experienced by a particle in the three-dimensional digitized Berea sandstone sample shown in Figure 1.

2.2.2 Anomalous dispersion

As outlined in the previous section, Brownian dynamics describes dispersion at times that are much larger than a typical correlation scale τ_c, which is equal to the transition time over an average pore length by the mean flow velocity. In order to scrutinize this condition, let us consider local transition times over the characteristic distance ℓ_c. According to (7), one can write

$$\tau = \int_s^{s+\ell_c} \frac{ds'}{v(s')} \approx \frac{\ell_c}{v}, \tag{11}$$

because $v(s')$ can be considered approximately constant over a distance ℓ_c which is of the order of the pore length (Saffman, 1959). This implies that the persistence time of particles with small velocities may be much larger than suggested by τ_c. Indeed, pore-scale velocity time series have been shown to display intermittent patterns. This means that they are characterized by long periods of small velocities and rapid fluctuations of large amplitudes (De Anna et al, 2013; Kang et al, 2014; Morales et al, 2017; Puyguiraud et al, 2019a), see also Figure 2. These patterns are indicative of a broad distribution of characteristic time scales. In fact, if the variance of τ is infinite, a sizeable amount of particles exhibits persistence times $\tau \gg \tau_c$. This means that particles do not become statistically equal over τ_c and thus invalidates the central assumption of the Brownian dynamics approach underlying Fickian dispersion. We will show below, that this property does not invalidate the existence of an REV.

Particle velocities vary on spatial scales imprinted in the medium structure rather than on a fixed times scale (Kang et al, 2014; Puyguiraud et al, 2019a). This property is naturally taken into account by continuous-time random walk (CTRW) and time-domain random walk (TDRW) transport models (Berkowitz et al, 2006; Painter

and Cvetkovic, 2005). In the framework of these random walk approaches, the particle motion along the mean flow direction is described by the following recurrence relations:

$$x_{n+1} = x_n + \frac{\ell_c}{\chi}, \qquad t_{n+1} = t_n + \tau_n, \tag{12}$$

where χ is the advective tortuosity (Koponen et al, 1996; Puyguiraud et al, 2019b), which measure the ratio of streamline length to average linear streamwise distance. The transition time is $\tau_n = \ell_c / v_n$. The particle velocities v_n are independent random variables. For $n = 0$, they are distributed according to an initial velocity distribution $p_0(v)$, which depends on the initial particle distribution. For $n \geq 1$, the v_n are identically distributed according to the flux-weighted Eulerian velocity distribution (Dentz et al, 2016)

$$p_s(v) = \frac{v p_e(v)}{\langle v_e \rangle}. \tag{13}$$

This has two consequences. First, at each random walk step particles can sample the full velocity spectrum, meaning that they are statistically equal. Second, the Lagrangian velocity statistics are stationary and ergodic. Particularly, particles evolve toward their stationary steady state distribution for distances larger than the length scale ℓ_c. For these conditions to hold, it is necessary that particles can sample a representative fraction of the Eulerian velocity distribution. Thus, in the following, we define the necessary and sufficient criteria required for the existence of a velocity REV in terms of the convergence of the velocity statistics with increasing support scale. Furthermore, we discuss the issue of ergodicity and stationarity.

2.3 Representative elementary volume

As discussed in the previous section, the representativeness of the velocity statistics sampled in the support volume and the existence of a stationary velocity distribution are key properties for transport upscaling for both Fickian and non-Fickian dispersion. Thus, the velocity statistics need to be representative of the (stationary) Eulerian velocity statistics in the medium for the support scale to be a transport REV. We note that a volume must first be an REV for porosity because the Eulerian velocity distribution may be linked to the pore size distribution (De Anna et al, 2017; Dentz et al, 2018) and thus, evolving porosity would cause evolving velocity statistics. If the sample is an REV for porosity, then the Eulerian velocity statistics may be representative. We define an REV in terms of the Eulerian velocity PDF in a similar manner as the porosity REV. A sample is considered to be a Eulerian REV if it is large enough for the Eulerian velocity distribution to become stationary. To quantify the evolution of the Eulerian velocity PDF in function of the support scale, the Eulerian velocity PDF is sampled on growing domains starting from a small volume in the center of the sample to the full sample volume. The spatially sampled PDF of the magnitude

of the flow velocity $v_e(\mathbf{x}) = |\mathbf{v}(\mathbf{x})|$ is defined as

$$p_\ell(v) = \frac{1}{\phi_\ell V_\ell} \int_{\Omega_\ell} d\mathbf{x} \delta\left[v - v_e(\mathbf{x})\right] \mathbb{I}(\mathbf{x} \in \Omega_f), \tag{14}$$

where Ω_ℓ is the physical domain on which the PDF is computed, and V_ℓ and ϕ_ℓ are its volume and its porosity, respectively. In order to quantify accurately the convergence of these distributions toward the Eulerian PDF $p_e(v)$ for the full sample, we define the distance between $p_\ell(v)$ and $p_e(v)$ based on the Kullback-Leibler (KL) divergence (Kullback and Leibler, 1951) as

$$d_{KL}(p_e, p_\ell) = \int_0^\infty dv p_\ell(v) \ln\left[\frac{p_\ell(v)}{p_e(v)}\right]. \tag{15}$$

The Kullback-Leibler divergence has been used to compare evolving PDFs to a reference distribution, (see for example Bigi, 2003; Robert and Sommeria, 1991; Lindgren et al, 2004). When $d_{KL} = 0$, the distributions are identical. Here we consider a threshold value of $\varepsilon = 10^{-2}$ as the criterion for when the support volume can be considered an REV.

2.4 Lagrangian ergodicity

As mentioned above, the convergence of the Eulerian velocity statistics on the support scale is not a sufficient condition for the upscaled random walk models to hold because these models assume by construction that particle velocities are sampled from the same stationary Lagrangian velocity PDF $p_s(v)$ at each except for the first step. In order to illustrate this, let us consider a porous media model consisting of a distribution of isolated straight capillaries. The support scale may be an REV for the Eulerian velocities. However, since the flow velocities are constant along streamlines, particles are never able to sample the full velocity spectrum.

The issue of Lagrangian ergodicity for pore scale flow has been studied in detail inPuyguiraud et al (2019a) in terms of the evolution of the s-Lagrangian velocity PDF, which is defined by

$$\hat{p}_s(v,s) = \int d\mathbf{a} \rho(\mathbf{a}) \delta[v - v(s,\mathbf{a})], \tag{16}$$

where $\rho(\mathbf{a})$ is the initial particle distribution. We measure convergence of $\hat{p}_s(v,s)$ toward the steady state $p_s(v)$ by the KL divergence $d_{KL}(\hat{p}_s, p_s)$.

2.5 Application to Berea sandstone sample

In this section we study the concept of the REV defined from the Eulerian velocity magnitude for the Berea sandstone sample illustrated in Figure 1 (Puyguiraud et al, 2019a), as well as ergodicity and stationarity of the Lagrangian velocity series. The advective tortuosity of the sample is $\chi = 1.64$ (Puyguiraud et al, 2019b).

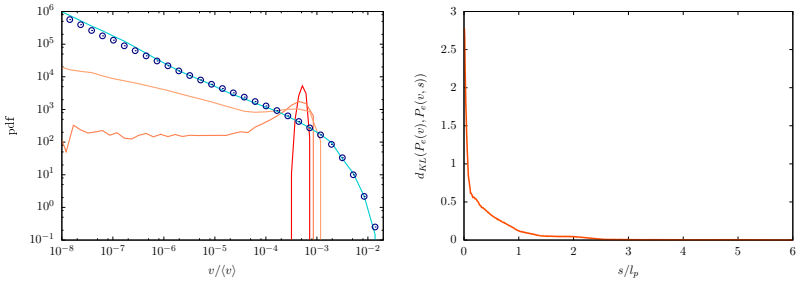

Fig. 3 (Left) The Eulerian velocity PDF computed on cubes centered in the middle of the sample of sizes $V = 4 \cdot 10^{-8} V_T$ (red solid line), $V = 1 \cdot 10^{-6} V_T$ (dark orange solid line), $V = 10^{-5} V_T$ (light orange solid line), $V = 1.25 \cdot 10^{-1} V_T$ (light blue solid line) and V_T (navy blue circles), where V_T is the bulk volume of the sample. (Right) The KL divergence between the full sample Eulerian velocity PDF and the Eulerian velocity PDFs computed on growing volumes from $V = 0$ to $V = V_T$.

First, we determine the porosity REV. Figure 1 displays the evolution of the ratio ϕ_ℓ between void and bulk volume computed on a size increasing domain that starts from a single point in the center of the sample to the total sample volume. The porosity starts from a value of one since the initial volume is situated in the void space. It then converges towards the porosity value of $\phi = 0.182$ after about $4.5\ell_p$, which means that the sample is an REV for porosity.

Second, we investigate the convergence of the Eulerian velocity statistics with increasing support scale. Figure 3a displays the Eulerian velocity PDFs respectively computed on cubes of volumes $V = 4 \cdot 10^{-8} V_T$, $V = 10^{-6} V_T$, $V = 10^{-5} V_T$, $V = 1.25 \cdot 10^{-1} V_T$, and V_T, where V_T is the bulk volume of the sample. We observe that the distribution evolves toward the full sample distribution as the volume of the cube increases. For $V = 4 \cdot 10^{-8} V_T$ we measure a small range of velocities. For $V = 10^{-6} V_T$ the distribution looks like the velocity distribution sampled in a single pore. The distribution sampled in a volume $V = 10^{-5} V_T$ corresponds to the average of several pore velocity distributions. Finally, the same statistics are observed for volumes $V = 1.25 \cdot 10^{-1} V_T$ and V_T, despite the former being 8 times smaller than the latter. To quantify accurately the convergence toward the Eulerian PDF, we use the aforementioned KL divergence between the successive $p_\ell(v)$ and $p_e(v)$. The distance between the full sample velocity PDF and the subsequent growing cubes velocity PDFs is displayed in Figure 3b. For small volumes V the KL divergence to the velocity PDF of the full sample is large since the volume only contains a restricted range of the velocity spectrum. Then, the KL divergence decreases quickly as the evolving distribution approaches the reference distribution. A distance $d_{KL} < 10^{-2}$ is reached for a volume $V \approx 0.125 V_T$. In other words, the limit distribution is attained. This indicates that the sample volume is noticeably larger than the Eulerian velocity REV.

We have seen that an REV for the Eulerian velocity magnitude exists. Now we investigate the stationarity of the velocity process by considering the evolution of $p_s(v,s)$ for a given initial velocity distribution $p_0(v)$ toward the steady state $p_s(v)$. To investigate accurately this evolution, we inject at the inlet particles in a given velocity range $v \in [v_l, v_u]$ and allocate the same weight to the whole range (see blue

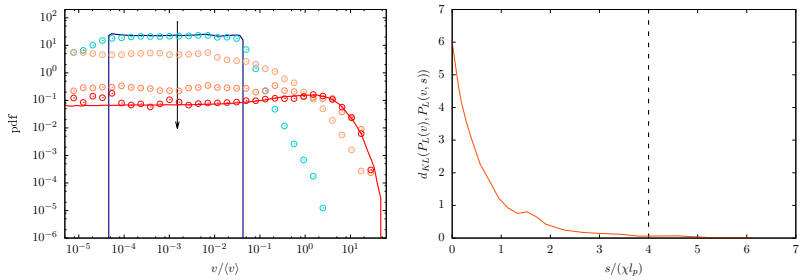

Fig. 4 (Left panel) The Lagrangian PDF $p_s(v,s)$ along an ensemble of streamlines measured at distance $s = \ell_p/15$ (light blue circles), $s = 4\ell_p/3$ (light orange circles), $s = 20\ell_p/3$ (dark orange circles) and $s = 32\ell_p/3$ (red circles. The blue solid line denotes the initial velocity PDF at $s = 0$ and the red solid line indicates the steady-state Lagrangian s-velocity PDF. (Right panel) The KL divergence (orange curve) between the steady-state Lagrangian velocity PDF and the successive Lagrangian velocity PDFs computed at increasing distances from $s = 0$ to $s = 10\ell_p$.

solid curve in the right panel of Figure 4). The resulting distribution is far from the steady-state distribution. We display the evolution of this distribution with distance in Figure 4a. The distribution converges toward the steady-state $p_s(v)$ after a distance of $s = 20\ell_p/3$.

As above we quantify convergence by computing the KL distance between the steady-state velocity PDF $p_s(v)$ and the distributions $p_s(v,s)$ computed after different distances s along the particle streamlines (see, also Puyguiraud et al, 2019a). The right panel of Figure 4 displays the evolution of the KL divergence with distance s along the streamline. At small distances the KL-divergence between $p_s(v,s)$ and the steady state $p_s(v)$ is large because the initial distribution is very different from the steady state distribution. The KL-divergence then decreases with increasing s, and reaches the threshold $\varepsilon = 5 \cdot 10^{-2}$ after $s = 20\ell_p/3$, which corresponds to an average linear distance of $4\ell_p$. Despite the fluctuations that we observe in $p_s(v,s)$ at distances $s \geq 20\ell_p/3$, we consider the convergence to be satisfactory because the KL divergence remains below ε. The small fluctuations are due to the complexity of the geometry that particles encounter. In conclusion the sample fulfills the stationarity conditions required for the upscaling.

3 Implications for Darcy Scale Transport

We have seen in the previous section that both Fickian transport descriptions in terms of Brownian dynamics as well as anomalous transport theories based on continuous time random walks require the existence of an REV in terms of the Eulerian velocity distribution. This is a necessary condition for the particle velocity series to be stationary and ergodic. Furthermore, we have seen that transport descriptions in terms of Brownian dynamics are valid at time scales that are much larger than the characteristic velocity correlation time. Thus, such approaches are only of limited applicability for situations characterized by broad distributions of the velocity persistence times

which are typical of natural porous media that display intermittent velocity time series. These features can be captured naturally by the CTRW approach. In this section we illustrate the CTRW approach to upscale pore-scale particle motion and discuss the implications for modeling hydrodynamic dispersion.

First, it is worth recalling that the previous sections focused on purely advective transport. This means, advective sampling of velocity contrast along streamlines is the only mechanism by which particles can experience the velocity heterogeneity and eventually become statistically equal, or in other words, for Lagrangian velocity statistics to become stationary and ergodic. In this sense, the purely advective case represents a worst case scenario because molecular diffusion is an additional sampling mechanism that makes particles experience the velocity contrast across streamlines, as in the problem of Taylor dispersion in a pipe (Taylor, 1953). In fact, diffusion impacts on pore scale transport in various various ways. Diffusive smoothing reduces the velocity contrast between particles, sets a maximum transition time over the length of a pore, and can lead to trapping in cavities and dead end pores (Saffman, 1959; Bijeljic and Blunt, 2006b; Dentz et al, 2018).

Thus, regarding the velocity sampling and the convergence toward stationarity, diffusion is favorable because it sets a maximum sampling time. Nevertheless, similarly to the purely advective case, a representative part of the velocity distribution needs to be available on the support scale. Thus, the presence of diffusion does not change the main conclusion regarding the existence and definition of the REV. Yet, it affects the stochastic particle dynamics because it introduces a temporal sampling mechanism in addition to the spatial sampling along streamlines. These aspects can be taken into account in the CTRW framework (Bijeljic and Blunt, 2006b; Dentz et al, 2018).

In the following, we briefly recall some basic relations of the CTRW. As described in Section 2.2.2, the CTRW models particle motion through the coupled space-time transitions (12). For purely advective particle motion, the transition time distribution $\psi(t)$ is given in terms of the stationary velocity distribution $p_s(v)$ as

$$\psi(t) = \frac{\ell_c}{t^2} p_s(\ell_c/t). \tag{17}$$

The impact of diffusion on velocity sampling, the introduction of a maximum transition time and trapping in cavities and low velocities zones can be modeled in terms of a coupled distribution $\psi(x,t)$ of transition lengths and times (Dentz et al, 2018,0). The evolution of the particle distribution $p(x,t)$ is given by the generalized master equation (Berkowitz et al, 2006)

$$\frac{\partial p(x,t)}{\partial t} = \int_0^t dt' \mathscr{K}(x-x',t-t') \left[p(x',t') - p(x,t') \right], \tag{18}$$

where the memory kernel $\mathscr{K}(x,t)$ is defined through its Laplace transform by

$$\hat{\mathscr{K}}(x,\lambda) = \frac{\lambda \hat{\psi}(x,\lambda)}{1-\hat{\psi}(\lambda)}, \tag{19}$$

Note that this formulation implicitly assumes that the transition lengths and times are stationary, this means the joint distribution of transition lengths and times for the first step is equal to $\psi(x,t)$, which in general may not be case, depending on the injection condition (Dentz et al, 2016). We notice that $p(x,t)$ is the particle density in a unit bulk volume. Thus, it is related to the concentration $c(x,t)$ in the fluid phase as $p(x,t) = \phi c(x,t)$. We assume that $\psi(x,t)$ is sharply peaked around the characteristic length scale ℓ_c. Thus one can expand the integrand on the right side of (18) up to second order in the displacement increment to obtain (Berkowitz et al, 2006)

$$\phi \frac{\partial c(x,t)}{\partial t} = -\int_0^t dt' \left[\mathscr{K}_v(t-t')\phi \frac{\partial c(x,t')}{\partial x} - \mathscr{K}_D(t-t')\phi \frac{\partial^2 c(x,t')}{\partial x^2} \right], \tag{20}$$

where we defined the advection and dispersion kernels in terms of their Laplace transforms as

$$\hat{\mathscr{K}_v} = \int dx x \hat{\mathscr{K}}(x,\lambda), \qquad \hat{\mathscr{K}_D} = \int dx x^2 \hat{\mathscr{K}}(x,\lambda). \tag{21}$$

Equations (18) and (20) describe in general non-Fickian transport (Berkowitz et al, 2006). In the absence of trapping and for times larger than the characteristic diffusion time scale ℓ_c^2/D (with D the molecular diffusion coefficient), the non-local advection-dispersion equation localizes and gives the advection-dispersion model (3) (Dentz et al, 2004).

Note that, since the REV is defined in terms of the Eulerian statistics inside the domain, the diffusion process has no impact on the REV definition and therefore does not affect its size. However, it will affect the times scales to reach ergodic conditions. Indeed, in a purely advective case particles sample velocities as they move along streamlines. In the presence of diffusion, particles can sample velocities additionally by changing streamlines, which may accelerate the convergence to a steady state distribution. Thus, defining the REV for purely advective transport guaranties its validity for any finite value of the Péclet number.

4 Conclusions

In this paper we aimed at answering the following question: Is there an REV for anomalous dispersion? We showed that an REV not only exists, but that its existence is also a necessary condition for CTRW approaches to non-Fickian hydrodynamic dispersion to be valid. The REV definition is set in terms of the Eulerian velocity statistics. Precisely, the REV scale is defined as the length scale of the sampling volume beyond which the spatially sample velocity distribution remains invariant. This definition requires the sample to be also a porosity REV since an evolving porosity would prevent the convergence of the Eulerian velocity distribution. The existence of an REV is a necessary conditions for the upscaling of anomalous dispersion using the CTRW approach. It requires the Lagrangian velocity series to form stationary stochastic processes that relaxes toward the stationary velocity distribution within a characteristic length scale. In other words, for a given sample a steady-state velocity

distribution needs to exist. In conclusion, if a sample fulfills these criteria, anomalous and as well as Fickian hydrodynamic dispersion can be upscaled by the CTRW approach.

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