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Is there a representative elementary volume for anomalous dispersion?

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Abstract The concept of the representative elementary volume (REV) is often as-7 sociated with the notion of hydrodynamic dispersion and Fickian transport. How-8 ever, it has been frequently observed experimentally and in numerical pore scale Q simulations that transport is non-Fickian and cannot be characterized by hydrody-10 namic dispersion. Does this mean that the concept of the REV is invalid? We investi-11 gate this question by a comparative analysis of the advective mechanisms of Fickian 12 and non-Fickian dispersion and their representation in large scale transport models. 13 Specifically, we focus on the microscopic foundations for the modeling of pore scale 14 fluctuations of Lagrangian velocity in terms of Brownian dynamics (hydrodynamic 15 dispersion) and in terms of continuous time random walks, which account for non-16 Fickian transport through broad distributions of advection times. We find that both 17 approaches require the existence of an REV that, however, is defined in terms of the 18 representativeness of Eulerian flow properties. This is in contrast to classical defini-19

- ²⁰ tions in terms of medium properties such as porosity, for example.
- 21 Keywords Representative elementary volume · upscaling · anomalous dispersion ·
- ²² continuous time random walks · velocity statistics

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23 1 Introduction

The notion of a representative elementary volume (REV) lies at the heart of macro-24 scopic (continuum) descriptions for systems that exhibit small scale structural disor-25 der (caused by the mixture of void and solid phases that forms the porous medium), 26 feature which is usually referred to as material heterogeneity. In the frame of con-27 tinuum approaches, the REV is associated to a point of the continuous field where 28 average properties, that are supposed to denote the effective properties of the mate-29 rial, are allocated. For instance permeability, from which the average fluid velocity 30 is derived, and hydrodynamic dispersion are critical properties for modeling steady 31 state flow and solute transport, respectively. The REV corresponds to the (minimum) 32 volume required to evaluate the effective properties of a heterogeneous material or, 33 in other words, the minimum volume above which the properties are stationary. This 34 is illustrated in Figure 1 for the ratio of void to bulk volume, i.e. the porosity, where 35 the REV size is determined from the constant limit value of ϕ_{ℓ} : 36

$$\boldsymbol{\phi}_{\ell} = \frac{1}{V_{\ell}} \int_{\boldsymbol{\Omega}_{\ell}} d\mathbf{x} \mathbb{I}(\mathbf{x} \in \boldsymbol{\Omega}_{f}), \tag{1}$$

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³⁹ where Ω_f and Ω_ℓ denote the fluid domain and bulk domain of volume ℓ , V_ℓ respec-⁴⁰ tively and $\mathbb{I}(\cdot)$ is the indicator function, which is equal to 1 if its argument is true and ⁴¹ 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 42 in a periodic microstructure, and 2) a volume containing a large set of micro-scale 43 structures displaying homogeneous and ergodic properties. The existence of the REV 44 relies on the existence of scale separation of spatial medium fluctuations. An REV 45 cannot be defined for continuously hierarchized heterogeneous media such as frac-46 tal materials. The REV is typically determined from applying this concept to the 47 material microstructure and specifically to its simplest quantitative notion, which is 48 its porosity (as illustrated in Figure 1). Porosity is easily measurable at laboratory 49 scale and can also be determined at pore-scale by using imaging methods such as 50 computed microtomography which allows characterizing the micro-structures over 51 volumes that are typically larger than the REV. Since the REV can be well-defined 52 for porosity, it is generally assumed that this definition also implies the existence 53 of transport relevant parameters such as the specific discharge and the hydrodynam-54 ics dispersion coefficients. The former represents the mean pore velocity, the latter 55 quantifies its fluctuations. The values of these parameters are considered to be well-56 defined and constant on the REV scale. Note that assuming the specific discharge 57 constant within the REV implies that the product of permeability and the pressure 58 59 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

⁶⁷ transport can be described by the advection-dispersion equation (ADE) (Bear, 1972)

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

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⁷⁰ This approach described Darcy-scale transport in terms of porosity ϕ , specific dis-⁷¹ charge *q* and the hydrodynamic dispersion coefficient \mathcal{D} .

Experimental (Moroni and Cushman, 2001; Cortis and Berkowitz, 2004; Holzner 72 et al, 2015; Morales et al, 2017) and numerical (Bijeljic and Blunt, 2006a; Bijeljic 73 et al, 2011; Liu and Kitanidis, 2012; De Anna et al, 2013; Kang et al, 2014; Meyer 74 and Bijeljic, 2016; Puyguiraud et al, 2019a; Dentz et al, 2018) pore scale studies 75 observed deviations from predictions based on the ADE (3). This includes tailing in 76 solute breakthrough curves, non-linear growth of dispersion and non-Gaussian par-77 ticle distributions and propagators. Such behaviors are usually modeled based on 78 non-local transport approaches such as multirate mass transfer and continuous time 79 random walks (Berkowitz et al, 2006; Noetinger et al, 2016) as well as fractional 80 dynamics (Cushman and Moroni, 2001). 81 In this paper, we investigate the notion of REV for non-Fickian dispersion. We 82

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.

⁸⁶ In Section 2.2.2 we discuss the framework of continuous time random walk models

(3)

and investigate what underlying assumptions they are relying on. This leads us to

⁸⁸ define, in Section 2.3 the Eulerian REV for anomalous transport and to illustrate its

⁸⁹ evaluation from computations performed using a digitized volume of a real rock sam-

₉₀ ple in Section 2.5. The implications of such an REV definition for continuum scale

⁹¹ modeling of Fickian and non-Fickian transport are discussed in section 3.

⁹² 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

⁹⁵ these considerations we propose the definition of an REV in terms of the Eulerian

⁹⁶ flow statistics, and discuss conditions on the Lagrangian velocity statistics.

97 2.1 Pore scale flow and transport

⁹⁸ 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

¹⁰³ 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 $t \rightarrow s$, with

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

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

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

¹¹⁶ 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.

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121 2.2.1 Fickian dispersion

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¹²² In order to identify the basic assumption underlying the ADE formulation of Darcy-¹²³ scale transport, we consider the Langevin equation (Gardiner, 2010) that is equivalent ¹²⁴ to the ADE (3),

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

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 pro-137 cess is based on several conditions. First, the velocity process needs to be stationary 138 and ergodic. This means that its mean and variance depend only on the time lag 139 and not on the absolute time. Second, velocity fluctuations decay exponentially fast 140 on a characteristic correlation time scale τ_c . Furthermore, based on the assumption 141 that the velocity distribution has finite variance, the displacement distribution, which 142 is the sum of random velocity increments, converges towards a Gaussian distribu-143 tion as time increases. This is a consequence of the central limit theorem (Gardiner, 144 2010) and warrants the modeling of the statistics of $v'_1(t)$ as Gaussian. The correla-145 tion model (9) is valid at observation times that are much larger than the correlation 146 scale τ_c , which can be related to the advection time over a characteristic length scale 147 ℓ_c , 148

$$\tau_c = \frac{\ell_c}{\overline{\nu}_1}.$$
(10)

This implies that for time $t \gg \tau_c$, particles must have access to the full spectrum of 151 velocity variability. The Langevin equation (8), which is valid at $t \gg \tau_c$, thus implies 152 that at each random walk step, particles can sample the full spectrum of random 153 velocities. Particles become statistically equal on the time scale τ_c . This temporal 154 notion can be related to a spatial REV scale through the length scale ℓ_c that is assumed 155 to mark the correlation time together with the mean velocity \overline{v}_1 . Thus, the REV scale 156 is supposed to contain a representative set of flow velocities that particles can sample 157 with equal probability. This is discussed further in Section 2.3. 158



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

159 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 .

¹⁶⁴ According to (7), one can write

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$$\tau = \int_{s}^{s+\ell_{c}} \frac{ds'}{v(s')} \approx \frac{\ell_{c}}{v},$$
(11)

because v(s') can be considered approximately constant over a distance ℓ_c which is 166 of the order of the pore length (Saffman, 1959). This implies that the persistence time 167 of particles with small velocities may be much larger than suggested by τ_c . Indeed, 168 pore-scale velocity time series have been shown to display intermittent patterns. This 169 means that they are characterized by long periods of small velocities and rapid fluc-170 tuations of large amplitudes (De Anna et al, 2013; Kang et al, 2014; Morales et al, 171 2017; Puyguiraud et al, 2019a), see also Figure 2. These patterns are indicative of 172 a broad distribution of characteristic time scales. In fact, if the variance of τ is in-173 finite, a sizeable amount of particles exhibits persistence times $\tau \gg \tau_c$. This means 174 that particles do not become statistically equal over τ_c and thus invalidates the central 175 assumption of the Brownian dynamics approach underlying Fickian dispersion. We 176 will show below, that this property does not invalidate the existence of an REV. 177

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 par ticle motion along the mean flow direction is described by the following recurrence
 relations:

$$x_{n+1} = x_n + \frac{\ell_c}{\chi},$$
 $t_{n+1} = t_n + \tau_n,$ (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 $n \ge 1$, the v_n are identically distributed according to the flux-weighted Eulerian velocity distribution (Dentz et al, 2016)

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

This has two consequences. First, at each random walk step particles can sample 196 the full velocity spectrum, meaning that they are statistically equal. Second, the La-197 grangian velocity statistics are stationary and ergodic. Particularly, particles evolve 198 toward their stationary steady state distribution for distances larger than the length 199 scale ℓ_c . For these conditions to hold, it is necessary that particles can sample a rep-200 resentative fraction of the Eulerian velocity distribution. Thus, in the following, we 201 define the necessary and sufficient criteria required for the existence of a velocity 202 REV in terms of the convergence of the velocity statistics with increasing support 203 scale. Furthermore, we discuss the issue of ergodicity and stationarity. 204

205 2.3 Representative elementary volume

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As discussed in the previous section, the representativeness of the velocity statistics 206 sampled in the support volume and the existence of a stationary velocity distribution 207 are key properties for transport upscaling for both Fickian and non-Fickian disper-208 sion. Thus, the velocity statistics need to be representative of the (stationary) Eule-209 rian velocity statistics in the medium for the support scale to be a transport REV. We 210 note that a volume must first be an REV for porosity because the Eulerian velocity 211 distribution may be linked to the pore size distribution (De Anna et al, 2017; Dentz 212 et al, 2018) and thus, evolving porosity would cause evolving velocity statistics. If the 213 sample is an REV for porosity, then the Eulerian velocity statistics may be represen-214 tative. We define an REV in terms of the Eulerian velocity PDF in a similar manner as 215 the porosity REV. A sample is considered to be a Eulerian REV if it is large enough 216 for the Eulerian velocity distribution to become stationary. To quantify the evolution 217 of the Eulerian velocity PDF in function of the support scale, the Eulerian velocity 218 PDF is sampled on growing domains starting from a small volume in the center of 219 the sample to the full sample volume. The spatially sampled PDF of the magnitude 220

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

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

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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

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

235 2.4 Lagrangian ergodicity

As mentioned above, the convergence of the Eulerian velocity statistics on the sup-236 port scale is not a sufficient condition for the upscaled random walk models to hold 237 because these models assume by construction that particle velocities are sampled 238 from the same stationary Lagrangian velocity PDF $p_s(v)$ at each except for the first 239 step. In order to illustrate this, let us consider a porous media model consisting of a 240 distribution of isolated straight capillaries. The support scale may be an REV for the 241 Eulerian velocities. However, since the flow velocities are constant along streamlines, 242 particles are never able to sample the full velocity spectrum. 243 The issue of Lagrangian ergodicity for pore scale flow has been studied in detail 244

inPuyguiraud et al (2019a) in terms of the evolution of the s-Lagrangian velocity
 PDF, which is defined by

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

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 $d_{KL}(\hat{p}_s, p_s)$.

251 2.5 Application to Berea sandstone sample

²⁵² 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,

²⁵⁴ 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).

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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 in-262 creasing support scale. Figure 3a displays the Eulerian velocity PDFs respectively 263 computed on cubes of volumes $V = 4 \cdot 10^{-8} V_T$, $V = 10^{-6} V_T$, $V = 10^{-5} V_T$ 264 $1.25 \cdot 10^{-1} V_T$, and V_T , where V_T is the bulk volume of the sample. We observe that the 265 distribution evolves toward the full sample distribution as the volume of the cube in-266 creases. For $V = 4 \cdot 10^{-8} V_T$ we measure a small range of velocities. For $V = 10^{-6} V_T$ 267 the distribution looks like the velocity distribution sampled in a single pore. The 268 distribution sampled in a volume $V = 10^{-5} V_T$ corresponds to the average of sev-269 eral pore velocity distributions. Finally, the same statistics are observed for volumes 270 $V = 1.25 \cdot 10^{-1} V_T$ and V_T , despite the former being 8 times smaller than the latter. To 271 quantify accurately the convergence toward the Eulerian PDF, we use the aforemen-272 tioned KL divergence between the successive $p_{\ell}(v)$ and $p_{\ell}(v)$. The distance between 273 the full sample velocity PDF and the subsequent growing cubes velocity PDFs is dis-274 played in Figure 3b. For small volumes V the KL divergence to the velocity PDF of 275 the full sample is large since the volume only contains a restricted range of the veloc-276 ity spectrum. Then, the KL divergence decreases quickly as the evolving distribution 277 approaches the reference distribution. A distance $d_{KL} < 10^{-2}$ is reached for a volume 278 $V \approx 0.125 V_T$. In other words, the limit distribution is attained. This indicates that the 279 sample volume is noticeably larger than the Eulerian velocity REV. 280

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 290 steady-state velocity PDF $p_s(v)$ and the distributions $p_s(v,s)$ computed after different 291 distances s along the particle streamlines (see, also Puyguiraud et al, 2019a). The 292 right panel of Figure 4 displays the evolution of the KL divergence with distance 293 s along the streamline. At small distances the KL-divergence between $p_s(v,s)$ and 294 the steady state $p_s(v)$ is large because the initial distribution is very different from 295 the steady state distribution. The KL-divergence then decreases with increasing s, 296 and reaches the threshold $\varepsilon = 5 \cdot 10^{-2}$ after $s = 20\ell_p/3$, which corresponds to an 297 average linear distance of $4\ell_p$. Despite the fluctuations that we observe in $p_s(v,s)$ at 298 distances $s \ge 20\ell_p/3$, we consider the convergence to be satisfactory because the KL 299 divergence remains below ε . The small fluctuations are due to the complexity of the 300 geometry that particles encounter. In conclusion the sample fulfills the stationarity 301 conditions required for the upscaling. 302

303 3 Implications for Darcy Scale Transport

³⁰⁴ We have seen in the previous section that both Fickian transport descriptions in terms

³⁰⁵ 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

³⁰⁷ distribution. This is a necessary condition for the particle velocity series to be station-

³⁰⁸ ary and ergodic. Furthermore, we have seen that transport descriptions in terms of

³⁰⁹ Brownian dynamics are valid at time scales that are much larger than the characteris-

tic 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 se-

ries. These features can be captured naturally by the CTRW approach. In this section

³¹⁴ 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 316 transport. This means, advective sampling of velocity contrast along streamlines is 317 the only mechanism by which particles can experience the velocity heterogeneity 318 and eventually become statistically equal, or in other words, for Lagrangian velocity 319 statistics to become stationary and ergodic. In this sense, the purely advective case 320 represents a worst case scenario because molecular diffusion is an additional sam-321 pling mechanism that makes particles experience the velocity contrast across stream-322 lines, as in the problem of Taylor dispersion in a pipe (Taylor, 1953). In fact, diffu-323 sion impacts on pore scale transport in various various ways. Diffusive smoothing 324 reduces the velocity contrast between particles, sets a maximum transition time over 325 the length of a pore, and can lead to trapping in cavities and dead end pores (Saffman, 326 1959; Bijeljic and Blunt, 2006b; Dentz et al, 2018). 327

Thus, regarding the velocity sampling and the convergence toward stationarity, 328 diffusion is favorable because it sets a maximum sampling time. Nevertheless, sim-329 ilarly to the purely advective case, a representative part of the velocity distribution 330 needs to be available on the support scale. Thus, the presence of diffusion does not 331 change the main conclusion regarding the existence and definition of the REV. Yet, 332 it affects the stochastic particle dynamics because it introduces a temporal sampling 333 mechanism in addition to the spatial sampling along streamlines. These aspects can 334 be taken into account in the CTRW framework (Bijeljic and Blunt, 2006b; Dentz 335 et al, 2018). 336

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)

$$\frac{\partial p(x,t)}{\partial t} = \int_{0}^{t} dt' \mathscr{K}(x-x',t-t') \left[p(x',t') - p(x,t') \right], \tag{18}$$

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

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

Note that this formulation implicitly assumes that the transition lengths and times 353 are stationary, this means the joint distribution of transition lengths and times for the 354 first step is equal to $\psi(x,t)$, which in general may not be case, depending on the 355 injection condition (Dentz et al, 2016). We notice that p(x,t) is the particle density in 356 a unit bulk volume. Thus, it is related to the concentration c(x,t) in the fluid phase as 357 $p(x,t) = \phi c(x,t)$. We assume that $\psi(x,t)$ is sharply peaked around the characteristic 358 length scale ℓ_c . Thus one can expand the integrand on the right side of (18) up to 359 second order in the displacement increment to obtain (Berkowitz et al, 2006) 360

$$\phi \frac{\partial c(x,t)}{\partial t} = -\int_{0}^{t} dt' \left[\mathscr{K}_{\nu}(t-t')\phi \frac{\partial c(x,t')}{\partial x} - \mathscr{K}_{D}(t-t')\phi \frac{\partial^{2} c(x,t')}{\partial x^{2}} \right], \quad (20)$$

where we defined the advection and dispersion kernels in terms of their Laplace trans-363 forms as 364

$$\hat{\mathscr{K}}_{\nu} = \int dx x \hat{\mathscr{K}}(x, \lambda), \qquad \qquad \hat{\mathscr{K}}_{D} = \int dx x^{2} \hat{\mathscr{K}}(x, \lambda). \qquad (21)$$

Equations (18) and (20) describe in general non-Fickian transport (Berkowitz et al, 367 2006). In the absence of trapping and for times larger than the characteristic diffusion 368 time scale ℓ_c^2/D (with D the molecular diffusion coefficient), the non-local advection-369 dispersion equation localizes and gives the advection-dispersion model (3) (Dentz 370 et al, 2004). 371

Note that, since the REV is defined in terms of the Eulerian statistics inside the 372 domain, the diffusion process has no impact on the REV definition and therefore 373 does not affect its size. However, it will affect the times scales to reach ergodic con-374 ditions. Indeed, in a purely advective case particles sample velocities as they move 375 along streamlines. In the presence of diffusion, particles can sample velocities addi-376 tionally by changing streamlines, which may accelerate the convergence to a steady 377 state distribution. Thus, defining the REV for purely advective transport guaranties 378 its validity for any finite value of the Péclet number. 379

4 Conclusions 380

In this paper we aimed at answering the following question: Is there an REV for 381 anomalous dispersion? We showed that an REV not only exists, but that its existence 382 is also a necessary condition for CTRW approaches to non-Fickian hydrodynamic 383 dispersion to be valid. The REV definition is set in terms of the Eulerian velocity 384 statistics. Precisely, the REV scale is defined as the length scale of the sampling vol-385 ume beyond which the spatially sample velocity distribution remains invariant. This 386 definition requires the sample to be also a porosity REV since an evolving porosity 387 would prevent the convergence of the Eulerian velocity distribution. The existence 388 of an REV is a necessary conditions for the upscaling of anomalous dispersion us-389 ing the CTRW approach. It requires the Lagrangian velocity series to form stationary 390 stochastic processes that relaxes toward the stationary velocity distribution within a 391 characteristic length scale. In other words, for a given sample a steady-state velocity 392

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³⁹³ distribution needs to exist. In conclusion, if a sample fulfills these criteria, anoma-

³⁹⁴ lous and as well as Fickian hydrodynamic dispersion can be upscaled by the CTRW

³⁹⁵ approach.

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400 References

- ⁴⁰¹ Bear J (1972) Dynamics of fluids in porous media. American Elsevier, New York
- ⁴⁰² Berkowitz B, Cortis A, Dentz M, Scher H (2006) Modeling non-fickian transport in
- geological formations as a continuous time random walk. Reviews of Geophysics
 44(2)
- Bigi B (2003) Using kullback-leibler distance for text categorization. In: European
 Conference on Information Retrieval, Springer, pp 305–319
- 407 Bijeljic B, Blunt MJ (2006a) Pore-scale modeling and continuous time
- random walk analysis of dispersion in porous media. Water Resources Research 42(1), 10.1029/2005WR004578, URL https://agupubs
- .onlinelibrary.wiley.com/doi/abs/10.1029/2005WR004578, https://
- agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/2005WR004578
- Bijeljic B, Blunt MJ (2006b) Pore-scale modeling and continuous time random walk
 analysis of dispersion in porous media. Water resources research 42(1)
- Bijeljic B, Mostaghimi P, Blunt MJ (2011) Signature of non-fickian solute transport
 in complex heterogeneous porous media. Phys Rev Lett 107(20):204,502
- ⁴¹⁶ Cortis A, Berkowitz B (2004) Anomalous transport in "classical" soil and sand ⁴¹⁷ columns. Soil Science Society of America Journal 68(5):1539, 10.2136/sssaj2004
- 418 .1539, URL https://doi.org/10.2136/sssaj2004.1539
- 419 Cushman JH, Moroni M (2001) Statistical mechanics with three-dimensional particle
- tracking velocimetry experiments in the study of anomalous dispersion. i. theory.
- Physics of Fluids 13(1):75-80, 10.1063/1.1328075, URL https://doi.org/10
 .1063/1.1328075
- ⁴²³ De Anna P, Le Borgne T, Dentz M, Tartakovsky AM, Bolster D, Davy P (2013) Flow
 ⁴²⁴ intermittency, dispersion, and correlated continuous time random walks in porous
 ⁴²⁵ media. Physical review letters 110(18):184,502
- 426 De Anna P, Quaife B, Biros G, Juanes R (2017) Prediction of velocity distribution
- from pore structure in simple porous media. Phys Rev Fluids 2:124,103, 10.1103/
 PhysRevFluids.2.124103
- 429 Dentz M, Cortis A, Scher H, Berkowitz B (2004) Time behavior of solute transport in
- heterogeneous media: transition from anomalous to normal transport. Adv Water
 Resour 27(2):155–173
- 432 Dentz M, Kang PK, Comolli A, Le Borgne T, Lester DR (2016) Continuous time
- random walks for the evolution of lagrangian velocities. Physical Review Fluids
- 434 1(7):074,004

435 Dentz M, Icardi M, Hidalgo JJ (2018) Mechanisms of dispersion in a porous medium.

Journal of Fluid Mechanics 841:851–882, 10.1017/jfm.2018.120, URL https:// doi.org/10.1017/jfm.2018.120

- 438 Gardiner C (2010) Stochastic Methods. Springer Verlag Berlin-Heidelberg
- 439 Holzner M, Morales VL, Willmann M, Dentz M (2015) Intermittent lagrangian ve-
- locities and accelerations in three-dimensional porous medium flow. Phys Rev E
 92:013,015
- 442 Kang PK, de Anna P, Nunes JP, Bijeljic B, Blunt MJ, Juanes R (2014) Pore-
- scale intermittent velocity structure underpinning anomalous transport through
- 3-d porous media. Geophysical Research Letters 41(17):6184–6190, 10.1002/
- ⁴⁴⁵ 2014GL061475, URL http://dx.doi.org/10.1002/2014GL061475
- ⁴⁴⁶ Koponen A, Kataja M, Timonen J (1996) Tortuous flow in porous media. Physical
 ⁴⁴⁷ Review E 54(1):406
- Kullback S, Leibler RA (1951) On information and sufficiency. The annals of math ematical statistics 22(1):79–86
- Lindgren B, Johansson AV, Tsuji Y (2004) Universality of probability density distributions in the overlap region in high reynolds number turbulent boundary layers.
- 452 Physics of fluids 16(7):2587–2591
- Liu Y, Kitanidis PK (2012) Applicability of the Dual-Domain Model to Nonaggregated Porous Media. Ground Water 50(6):927–934
- Meyer DW, Bijeljic B (2016) Pore-scale dispersion: Bridging the gap between micro scopic pore structure and the emerging macroscopic transport behavior. Physical
 Review E 94(1):013,107
- 457 Review E 94(1).013,107
- ⁴⁵⁸ Morales VL, Dentz M, Willmann M, Holzner M (2017) Stochastic dynamics of inter ⁴⁵⁹ mittent pore-scale particle motion in three-dimensional porous media: Experiments
 ⁴⁶⁰ and theory. Geophysical Research Letters 44(18):9361–9371
- 461 Moroni M, Cushman JH (2001) Statistical mechanics with three-dimensional par-
- ticle tracking velocimetry experiments in the study of anomalous dispersion. II.
- experiments. Physics of Fluids 13(1):81–91, 10.1063/1.1328076, URL https://
 doi.org/10.1063/1.1328076
- Noetinger B, Roubinet D, Russian A, Le Borgne T, Delay F, Dentz M, De Dreuzy
 JR, Gouze P (2016) Random walk methods for modeling hydrodynamic transport
 in porous and fractured media from pore to reservoir scale. Transport in Porous
- Media pp 1–41
- Painter S, Cvetkovic V (2005) Upscaling discrete fracture network simulations:
 An alternative to continuum transport models. Water Resour Res 41:W02,002,
 10.1029/2004WR003682
- Puyguiraud A, Gouze P, Dentz M (2019a) Stochastic dynamics of lagrangian pore-scale velocities in three-dimensional porous media. Water Resources
- Research 55, 10.1029/2018WR023702, https://agupubs.onlinelibrary
 .wiley.com/doi/pdf/10.1029/2018WR023702
- Puyguiraud A, Gouze P, Dentz M (2019b) Upscaling of anomalous pore-scale dis persion. Transport in Porous Media
- 478 Robert R, Sommeria J (1991) Statistical equilibrium states for two-dimensional
- 479 flows. Journal of Fluid Mechanics 229:291–310, 10.1017/S0022112091003038

Saffman P (1959) A theory of dispersion in a porous medium. Journal of Fluid Me chanics 6(03):321–349

- 482 Taylor G (1953) Dispersion of soluble matter in solvent flowing slowly through a
- tube. Proceedings of the Royal Society of London Series A, Mathematical and
- Physical Sciences 219(1137):186–203, URL http://www.jstor.org/stable/

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