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Stretching and folding sustain microscale chemical gradients in porous media

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11 Fluid flow in porous media drives the transport, mixing and reaction of molecules, particles and microorganisms across a wide spectrum 1213of natural and industrial processes. Current macroscopic models that average pore-scale fluctuations into an effective dispersion co-14 15efficient have shown significant limitations in the prediction of many 16 important chemical and biological processes. Yet, it is unclear how 17three-dimensional flow in porous structures govern the microscale 18 chemical gradients controlling these processes. Here we obtain 19 high-resolution experimental images of microscale mixing patterns 20in three-dimensional porous media and uncover an unexpected and 21general mixing mechanism that strongly enhances concentration 22gradients at pore-scale. Our experiments reveal that systematic 23stretching and folding of fluid elements are produced by grain con-24tacts, through a mechanism that leads to efficient microscale chaotic 25mixing. These insights form the basis for a general kinematic model 26linking chaotic mixing rates in the fluid phase to the generic struc-27tural properties of granular matter. The model successfully predicts 28the resulting enhancement of pore-scale chemical gradients, which 29appear to be orders of magnitude larger than predicted by dispersive 30 approaches. These findings offer new perspectives for predicting 31 and controlling the vast diversity of reactive transport processes in 32natural and synthetic porous materials, beyond the current disper-33sion paradigm. 34

Porous Media | Mixing | Lagrangian Chaos 35

37 Introduction

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luid mixing in porous media plays a key role in a range 39 of natural and industrial systems (1-3). In these confined 40 environments, mixing enables or limits reactions controlling 41 the degradation of contaminants in the subsurface, the cycles 42of biogeochemical elements such as nitrogen, iron and carbon, 43and the sequestration of CO_2 in deep reservoirs (4–10). Mixing 44 also shapes the nutrient landscapes and chemical gradients 45seen by bacteria evolving in soils or medical systems (11, 12)46 and facilitates chemical processes in drug delivery, packed 47bed reactors, flow batteries, or catalysts (13-15). Increasing 48 evidence of sustained chemical gradients and incomplete mix-49 ing below the pore-scale, along with associated impacts upon 50chemical reactions (3, 16-18), have questioned the relevance of 5152 macroscopic dispersion coefficients to capture these processes (1). Yet, it is currently unknown how three-dimensional flow 53topologies in porous structures control microscale mixing rates 54and concentration gradients. 55

56Recent theories (19, 20) have suggested that laminar flow 57 through three-dimensional porous media may possess the basic ingredients for chaotic advection, which would represent a pos-58 sible mechanism for the enhancement of microscale chemical 59 gradients, and the persistence of incomplete mixing at the 60 pore-scale. These chaotic dynamics may have particularly 61 important consequences for microbial processes, a broad range 62

of which are hosted in porous environments (21). Biological processes in turbulent flows have been shown to be deeply altered by chaotic advection, which promotes coexistence of competitive microbial species (22) and affects the chemotactic responses of micro-organisms (23). However, whether such chaotic dynamics can spontaneously develop in laminar flows through porous media remains on open question.

A key experimental barrier to the direct imaging of solute advection in three-dimensional porous materials is their predominantly opaque nature. Whilst X-ray micro-tomography technologies have progressed significantly (24), they still cannot resolve the fine structures produced below pore-scale. In contrast, use of visible spectrum refractive index matching between the solid and the fluid phases represents a viable alternative to observe solute mixing, as obtained with hydrogel beads in water (25). However, as molecular diffusion eventually masks the deformation of dyed fluid elements, a direct measurement of fluid deformation in random porous media is an outstanding challenge. Here we overcome these limitations by performing high-resolution laser imaging of the evolution of a low diffusivity fluorescent dye plume through a column of optically transparent borosilicate spheres via high precision refractive index matching (Fig. 1). This technique allows reconstruction of the three-dimensional dye plume at unprecedented resolution, thus providing direct experimental observation of pore-scale fluid deformation and mixing in

Significance Statement

Porous media flows are central to environmental, industrial, and biological systems, where they transport molecules, particles, and microorganisms and trigger important bio-geo-chemical reactions. There is increasing evidence that many of these processes are highly sensitive to chemical gradients below the pore-scale. But it is unknown how porous architectures control microscale concentration heterogeneities. Here, we provide high-resolution experimental images that fully resolve 3D porescale mixing dynamics. We show that grain contacts control the folding of fluid elements in the pore-space, which, in addition to fluid stretching as stagnation points, leads to the exponential enhancement of microscale concentration gradients. We use these insights to derive a kinematic model linking mixing rates to pore geometry, opening new perspectives for reactive transport modelling.

The authors declare no competing interests.

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¹¹⁹ J.H did the experiments, the data analysis and model and wrote the paper. D.R.L. and Y.M. contributed to data and model interpretation and redaction. RT performed the numerical simulations discussed in section A of the S.I. T.L.B formulated the idea and contributed to analysis, interpretation and redaction.



porous media. These novel data reveal the hitherto unknown role of grain contacts in controlling folding and stretching of fluid elements, a mechanism that generates strong chaotic advection and significantly enhances chemical gradients at the microscale. Since grain contacts are inherent to all granular porous materials, we deduce that chaotic mixing is ubiquitous in flow through all such materials, potentially impacting a large range of fluid-borne phenomena in natural and engineered systems.

3D imaging of mixing patterns in porous media

We observed three-dimensional fluid deformation and solute mixing in laminar flows through monodispersed random bead packs of diameters d = 7, 10 and 20 mm, optically matched into a glycerol-water fluid mixture (Fig. 5). A fluorescent dye is continuously injected upstream of the transparent column as a thin tube of radius $L_0 \ll d$ (Fig. 2a), and advected downstream by the porous flow at the mean longitudinal advection velocity u. Cross-stream concentration patterns of the dye plume are imaged in the pore-space via a translational scan using a laser sheet and a camera. The dye cross-section rapidly evolves into a highly elongated (Fig. 2b) and striated filamentous structure (Fig. 2c) due to transverse stretching and folding of fluid elements in pores (SI Videos S1, S2, S3). The combination of a highly viscous fluid mixture and a high molecular weight dye results in laminar flows of low diffusivity, characterized by Reynolds numbers on the order of $Re=7 \cdot 10^{-3}$ and Péclet numbers on the order of $Pe=10^4$ (SI Table S1). The deformation of the dye plume (Fig. 1a) thus closely shadows that of the advected fluid, facilitating direct visualization of pore-scale fluid deformation. We use spline fitting on the 177178images to reconstruct the backbone of the cross-sectional dye footprint, called a filament, and estimate its total length L(x)179for 9 to 14 bead diameters downstream from the injection 180181point (see Fig. 2, SI Video S3).

182 The mean total filament elongation L/L_0 , averaged over the 183 18 statistically equivalent packings (*SI Table* S1), exhibits clear 184 exponential growth with normalized longitudinal distance x/d185 (Figure 3). The dimensionless exponent $\mu \equiv \ln(L/L_0)/(x/d) =$ 186 0.29 ± 0.01 is independent of both bead diameter and flow

188Fig. 1. (a) Experimental dye plume 189with backbone filament (red lines) at 190selected stages of the folding mechanism (run III, SI Video S4). Beads 191 have been shrunk by 40% and white 192lines depict the contact line joining 193bead centres; surrounding beads are 194not shown. (b) Cross-sections detail-195ing the typical folding stages (run I, SI Video S3). Upon passing the contact 196point 1-2 (b.0), the filament is stretched 197 (diverging arrows) along the contact 198plane (dashed line) and compressed 199in the perpendicular direction (converg-200ing arrows). After contact (b.1), the directions of stretching and compres-201sion are inverted, and a cusp forms. 202creating a fold (b.2) which is advected 203over the subsequent contact 3-4 (b.3). 204Other experimental runs and numerical simulations are reported in SI Figures 205S1. Fig. S2 and SI Video S5. 206

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rate and is known as the *topological entropy* of the flow (26). Via the central limit theorem, μ is related to the mean λ and variance σ_{λ}^2 of the dimensionless stretching rate (see Methods) 211

$$\mu = \lambda + \sigma_{\lambda}^2 / 2. \tag{1} \begin{array}{c} 212\\213 \end{array}$$

The dimensionless parameter λ is also known as the Lyapunov 214215exponent (26), which can be converted into a mean stretching 216rate per unit time as $\lambda u/d$. In addition to stretching, the 217filament also undergoes highly localised folding events which 218result in closely foliated striations (Fig. 2c). These fluid defor-219mations are the hallmarks of chaotic mixing, and permit thus 220permitting exponential elongation of material elements in a 221finite-sized domain. 222

The role of grain contacts in folding

Folding of dye filaments is consistently initiated downstream of 225contact points between two beads (Fig. 1b and SI Figure S1). 226 The cusp-shaped geometry near grain contacts means that 227when crossing a contact point (b.0), fluid elements are first 228 compressed in the direction joining the two bead centres and 229stretched in the perpendicular direction. Downstream of the 230contact point, the direction of compression and stretching are 231exchanged and a cusp forms locally in the dye filament (b.1). 232This cusp is stretched in the following pore space, leading to 233a folded filament made of two straight segments (b.2). This 234stretching and folding process is repeated sequentially as the 235folded filament encounters other contact points (b.3), leading 236to thin solute dve foliations that are the hallmarks of chaotic 237advection (26) (Fig. 2c). 238

Recent studies (19, 20) identified the role of separation and 239reattachment points on open grain boundaries (saddle points) 240in generating exponential stretching of fluid elements. Here, we 241uncovered the distinct role of contact points between grains in 242 generating systematic folding of fluid elements. Simulations of 243laminar flow in periodic bead packings (see *SI Text* section A) 244show that attracting and repelling stream surfaces (unstable 245and stable manifolds) produced by these saddles indeed control 246stretching of material lines in the pore space. We found that 247these manifolds intersect orthogonally at grain contacts (SI 248

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Fig. 2. Cross-stream sections of the fluorescent dye plume at increasing distances 268 from the injection: x/d = 0 (a), 3.2 (b) and 9.3 (c)(run II, SI Video S1 and S2). 269Colors represent local dye concentrations. Beads appear in deep blue. A spline curve 270(dotted black lines) is used to fit the filament backbone on each cross-section image: 271from which the total filament length L is obtained. 272

Figure S2 and SI Video S5), where both the local flow velocity 274and the stretching rate vanish and manifold stabilities are 275exchanged, so that repelling stream surfaces become attracting 276and vice-versa. Hence, over a contact point, the local flow 277structure imparts finite curvature to fluid elements, which 278results in the sharp folds observed experimentally (Fig. 1) 279The repetition of this basic stretching and folding sequence over 280281successive contact points offers a simple geometric framework to relate stretching rates to granular structure. 282

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284Linking stretching statistics to the porous structure

285Sharp folding of dye filament in between contact points pro-286duces a number n_c of localised cusps of strong curvature, 287 separated by straight segments of moderate curvature (Fig. 6). 288We define the mean segment length as $L_c = L/n_c$ and the 289average area swept out by a segment between two succes-290sive contact points as $S_c = S/n_c$, where S is the total area 291swept by the filament. We find that L_c and S_c both converge 292to stationary values (inset of Figure 3). Hence, the average 293advection distance between two successive contact points is 294statistically constant and equal to $X_c = S_c/L_c \approx 3.45 d$. Over 295this distance, a single elementary segment folds, giving rise to 296two new straight elementary segments. Thus, over the same 297distance, its length $\ell(X)$ must doubles to maintain $\langle \ell \rangle = L_c$ 298constant, so that $\ell(X) = 2^{(X/X_c)}$. Hence, the average dimen-299sionless stretching rate λ of elementary fluid segments can be 300 estimated as 301

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$$\lambda \equiv \frac{\mathrm{d}(\log \ell)}{\mathrm{d}(X/d)} = \frac{\log 2}{X_c/d} \approx 0.21.$$
 [2]

This rate is larger than found in synthetic porous media, 305 306 such as random pore networks ($\lambda \approx 0.12$ (19)) and body centered cubic assemblies of spheres ($\lambda \approx 0.128$ (27)), reflecting 307the remarkably efficient stretching and folding process occur-308 309 ring in random granular media. The variance of the stretching 310 rate can be estimated from Eq. (1) as $\sigma_{\lambda}^2 \approx 0.16$, a value



315Fig. 3. Total filament 316elongation L/L_0 with 317respect to the nor-318 malized pore advection distance $\boldsymbol{x}/\boldsymbol{d}$ from 319the dye injection point. 320 Inset: Convergence 321of the mean segment 322length $L_c = L/n_c$ and area $S_c = S/n_c$ 323toward constant val-324ues, with n_c , the num-325326

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comparable to the mean stretching rates λ , as it is typically the case in space-filling chaotic flows (28).

330 As shown by Eq. (2), the strength of chaotic advection is entirely governed by the spatial frequency X_c^{-1} with which 331segments encounter grain contacts. We show in Methods 332that in isotropic packings $X_c \approx 8 \log 2\phi z_c d_p/3$, with z_c the 333 coordination number (the mean number of contacts per bead), 334 ϕ the solids volume fraction and d_p the mean pore diameter. 335This yields a simple geometric estimate of the dimensionless 336 337 Lyapunov exponent

$$\lambda \approx \frac{3}{8} \frac{\phi z_c d_p}{d}.$$
 [3]
$$\begin{array}{c} 338\\ 339\\ 340 \end{array}$$

Equation 3 is applicable to non-isotropic packings with a prefactor that quantifies the distribution of orientations of the contact lines joining bead centres with respect to the mean flow direction (see Methods). Insertion of the experimental values $z_c = 6$, $\phi = 0.5$ and $d_p/d = 0.24$ in Eq. (3) yields $\lambda \approx$ 0.27 which is in reasonable agreement with the experimental estimate of 0.21, given the slight anisotropic nature of our experimental packings (see Methods). Equation 3 provides the first quantitative link between microscopic fluid stretching rates and porous media structural properties.

Discussion

353Stretching and folding sustain microscale chemical 354gradients. Repeated sequences of stretching and folding 355leads to exponential compression of fluid elements that can 356 sustain concentration gradients at the pore-scale (Fig. 2). 357 These concentration gradients are locally controlled byé the 358 balance between diffusive spreading rate $(D_{\rm m}/s^2)$, with $D_{\rm m}$ the 359molecular diffusivity, and the mean compression rate $(\lambda u/d)$, 360which is equal to the stretching rate in steady incompressible 361 flows. These two rates equilibrate at the Batchelor scale 362

$$a_B = \sqrt{D_{\rm m} d / (\lambda u)}, \qquad [4] \quad 363$$

which represents characteristic length scale of solute concentration fluctuations. Pore-scale mixing is thus characterized by the dimensionless length scale $s_B^* = s_B/d$, which is related to the macroscopic Péclet number $Pe = ud/D_m$ as,

$$s_B^* = (\lambda \text{Pe})^{-1/2}.$$
 [5] 369
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For $s_B^* > 1$, the length scale of solute concentration fluc-371tuations are larger than the grain diameter and therefore 372 373 concentration fields are expected to be well-mixed at the 374pore-scale. Our estimation of the Lyapunov exponent λ 375 implies that the transition to incomplete pore-scale mixing 376occurs at Péclet number above 5, values commonly encoun-377tered in many natural and industrial contexts (29). This 378suggests that a broad range of biogeochemical processes are 379 possibly affected by incomplete pore-scale mixing and chaotic 380 advection. From results established on chemical and microbial 381processes in turbulent and chaotic flows at comparable mixing 382rates (22, 23), it is possible to anticipate a range of possible 383 effects of chaotic mixing in porous media, including altered 384effective kinetics and microbial growth dynamics, increased 385biodiversity and enhanced benefit of sensing. Because they 386 can only develop in three-dimensional topologies under 387 steady conditions (26), these chaotic dynamics are generally absent in quasi two-dimensional microfluidic experiments 388389used to investigate the microscale interactions between flow, 390 concentration gradients, chemical reactions and microbial 391processes (3, 11, 30). Novel experiments in three-dimensional 392porous media and new modelling frameworks are thus needed 393to explore these dynamics.

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395Microscale mixing model. The experiments in this 396 study have used high Péclet numbers to uncover the rate 397 and kinematics of mixing in porous media. These results 398 may be extended to prediction of macrosocopic mixing rates 399 and concentration statistics at arbitrary Peclet numbers 400via lamellar mixing models that couple stretching and 401diffusion (31-33). In SI Text section C, we derive such 402mixing model and compare its predictions in terms of dye 403 concentration statistics to the experimental data. The lamellar 404model successfully captures the measured exponential decay 405of the mean maximum solute concentration of dye filaments 406 with longitudinal distance $c_{\rm max} \sim \exp(-(\lambda + \sigma^2/2)x/d)$ 407(Fig. 4), as well as the growth of concentration fluctuations 408caused by variability of the Lagrangian stretching history. 409These predictions provide an independent validation of the 410 estimated mean and variance of the stretching rate, $\lambda \approx 0.21$ 411 and $\sigma_{\lambda}^2 \approx 0.16$. In contrast, conventional mixing models 412based upon macroscopic dispersion coefficients (1) ignore 413incomplete mixing at the pore-scale and predict an algebraic 414 decay of concentrations $c_{\max} \sim (x/d)^{-1/2}$ (SI Text section B). 415From the normalized Batchelor scale (Eq. (5)), pore-scale 416concentration fluctuations predicted by the lamellar model will 417persist for all Péclet numbers larger than five. In this range, 418macroscopic dispersion models fails to resolve pore-scale 419concentration gradients, leading to incorrect predictions of 420a broad range of reactive transport dynamics (3, 16-18). 421Coupling lamellar mixing models with reactive processes is 422 therefore a promising avenue to capture the effect of pore-scale 423 incomplete mixing on biogeochemical dynamics. 424

426**Porous materials as mixers.** From Eq. (3), the mixing efficiency of steady laminar flows through random bead 427 packs (defined as the ratio of the average stretching rate to 428429the average strain rate) is found to be 3% (SI Text section D). This value is comparable to the performance of industrial 430mixers (26) and an order of magnitude larger than that of 431micro-fluidic chaotic mixers (34), thus opening new opportu-432nities for exploiting the mixing properties of porous materi-433als. Chaotic advection is known to both increase dispersion 434



Fig. 4. Experimental average (triangles) and standard deviation (circles) of the local
maximum concentration c_{max} along x. Values are normalized by the initial maximum
concentration c_0 . Classical model predictions are shown as black dashed and dotted
lines. Lamellar mixing model predictions for the average and standard deviation of
 c_{max} are shown respectively as the green dotted line and the purple continuous line
(see SI Text sections B and C for derivations).452
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458transverse to the mean flow direction and retard longitudinal 459dispersion (35). It also alters the transport of finite-sized 460particles such as colloids and micro-organisms (36) and may 461 thus control their clustering in the pore space and deposition 462on grain boundaries. In relating stretching rates to the porous 463micro-structure, Eq. (3) offers a possible pathway to the design 464of engineered porous materials with optimum mixing charac-465teristics. This concept may find important applications in 466 the design of heat exchangers, packed bed filters and reactors, 467 where transverse dispersion and mixing act to enhance pro- 468 cess efficiency, and for continuous flow chemistry (15), such 469 as pressure-driven chromatography, where product selectivity 470 and yield strongly depends upon the minimization of longi- 471 tudinal dispersion. These applications would first require a 472 validation Eq. (3) over a large range of packing geometries. 473474

Conclusions

Using high resolution experimental imaging of microscale mix- 477 ing in three-dimensional granular media we have demonstrated 478 the existence of efficient stretching and folding of fluid elements 479at the pore-scale. We use these insights into the kinematics of 480 mixing to develop a stochastic model for the prediction of the 481 Lyapunov exponent from the geometric properties of the grain 482pack, and validate this model against experimental observa-483tions. The formalization of these observations into a chaotic 484 mixing model, coupling stretching and diffusion, demonstrates 485that incomplete mixing persists at pore-scale for Péclet num-486 bers above five. This model captures the processes governing 487 microscale chemical gradients, opening new perspectives for 488 understanding, predicting and controlling a large spectrum of 489 physical, chemical, and biological processes, in natural and 490 engineered porous systems. 491

The discovery of systematic and efficient chaotic mixing 492 in single phase laminar flows through random bead packs— 493 the archetype of porous media—calls for deeper investigation 494 of this phenomenon in a broad range of systems, including 495 polydisperse packings, consolidated soils and rocks, and more 496

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497 complex flows, such as multiphase, inertial or non-Newtonian 498 flows. While these cases may act to modify the rate of mixing, 499 the fundamental kinematics described in this study should 500 persist as they arise from basic fluid-grain interactions. The 501 investigation of these system-specific modulations of chaotic 502 mixing in porous matter form promising research perspectives. 503

504 Materials and Methods

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506507Experimental protocol. The porous column consists of a verticallyoriented rectangular column of cross section 48×48 mm (Fig. 5), 508containing monodisperse borosilicate glass beads (Sigmund Lindner 509GmbH) of diameter d = 7,10 or 20mm that are loosely and randomly 510packed via gravitational settling. The pore space between the beads 511is filled with a glycerol-water mixture (1.4%w/w water) at controlled 512temperature (T= 25° C). Fluid flow is driven by a constant pressure difference imposed between the inlet and outlet ports, respectively 513at the top and bottom of the column. The flow rate is continuously 514monitored at the outlet by a scale. Together with the knowledge of 515the packing porosity, this provides an estimate of the mean pore 516velocity, u. To visualize fluid flow and deformation through the bead 517pack, a solute fluorescent dye (PromoFluor-488LSS) is continuously injected in the upper part of the cell through a needle of internal 518diameter $L_0 = 0.5 \,\mathrm{mm}$. The injected dye develops into a steady 519plume downstream of the injection point. The mean flow velocity u520is chosen to be sufficiently low to get small Reynolds numbers and laminar flows (Re= $ud/\nu \approx 5 \cdot 10^{-3} \ll 1$, where $\nu \approx 700$ cP is the 521kinematic fluid viscosity), and fast enough for the dye Péclet number 522to be large and for fluid deformation to be measured from the dye 523backbone (Pe= $ud/D_{\rm m} \approx 8.6 \cdot 10^3$, where $D_{\rm m} \approx 2 \cdot 10^{-11} \text{ m}^2 \text{s}^{-1}$ is 524the molecular diffusivity of the dye in the glycerol-water mixture). 525For representativeness, experiments are repeated for multiple dye 526injection locations and for various packing realisations and bead diameters, as summarised in SI Table S1. The coordinates of 527the bead centres are determined via a three-dimensional Hough 528transform on the image stack obtained by the translational laser 529scan, where the background fluid fluorescence allows distinguishing 530the grains. From these coordinates, several structural properties of the porous media are obtained : ϕ , the solid volume fraction 531(the ratio of volume occupied by the beads over the total column 532volume); z_c , the coordination number (the number of neighbouring 533beads whose centres lie $d \pm 5\%$ away from the reference bead); d_p , 534the mean diameter of the largest sphere inscribed in the pore space, 535obtained by a distance transform computed on a voxelized image of the fluid phase. 536

537Reconstruction of the dye filament backbone. In each cross-stream 538section of the solute dye plume, a one-dimensional backbone of the 539dye filament is reconstructed via the adjustment of spline curves and its total length L is computed (Fig.2 and Fig. 6a). In experimental 540run II (Fig. 2 and SI Video S1), the tracking is possible until 541downstream distance x = 9.27 d (beyond which the diffusive filament 542merges with itself), corresponding to a total elongation of $L/L_0 \approx$ 543167 (Fig.2c), where L_0 is the initial length of the dye filament 544backbone.

545Distribution of elongations. The sequential stretching and folding 546process leading to exponential growth of the total filament back-547bone length L implies that the length l of a fluid element follows 548a multiplicative random process (28, 32), such that l grows as $dl/dx^* = \gamma l$, where $x^* = x/d$ and γ is a random, statistically sta-549tionary stretching rate of mean λ and variance σ_{λ}^2 . The length l thus results from the product of the successive stretching rates γ , 550551such that $\log l$ is the sum of a series of independent and identically 552distributed random variables. From the central limit theorem, the 553distribution of $\log l$ must then converge with downstream distance towards a normal distribution of mean $\lambda x'$ and variance $\sigma_{\lambda}^2 x^*$. This 554convergence is obtained after a few bead diameters since i) the 555dye filaments length increase exponentially and thus sample an 556increasingly large number of independent stretching rates in the 557pore space and ii) the stretching rates are distributed within pores, 558so that several independent stretching rates are experienced over Camera Linear displacement stage Distance trout in the constraint of the constraint

561Fig. 5. Experimental setup for 562three-dimensional imaging of the 563mixing of a fluorescent solute 564dye in optically matched porous 565bead packs. The dye is contin-566uously injected through a thin needle upstream of the gran-567ular column, while maintaining 568a steady background laminar 569flow. After stabilisation of the 570solute dye plume, transverse 571cross-sections of concentrations are obtained by displacing a 572laser sheet (Oxxius, wavelength 573488 nm, beam waist 50 µm) in 574the x direction while recording 575the emmited fluorescence with 576a CMOS camera (Hamamatsu ORCA-Flash4.0 16bits) mounted 577 with a band pass filter (Midopt 578BN532) and oriented at an an-579gle of 45 degrees from the laser 580plane. The perspective view is then ortho-rectified by a projec-581tive transform 582

a unit diameter distance. The mean value of l is thus such that $\langle l \rangle \sim \exp(\mu x^*)$ with $\mu = \lambda + \sigma_{\chi}^2/2$, which sets the growth rate of the total filament length to $\langle L/L_0 \rangle = \exp(\mu x^*)$.

Number of high curvature regions. As shown in Fig. 1b, when the filament is advected through contact points between beads, localized regions of very high curvature develop in the filament backbone. We define cusps as isolated regions of the filament backbone where the curvature κ of the spline curve exceeds the threshold $\kappa = 10^3 d^{-1}$. We find (Fig. 6c) that the total number n_c of cusps in the filament backbone increases exponentially with the downstream distance x/d at a rate similar to that of the total filament length L. This suggests that stretching and folding events occurs in proportion of each other and that the resulting process is statistically stationary.

Prediction of the mean stretching rates from the porous media prop-597 erties. Based on the consistently observed sequence of stretching 598and folding in the pore space and its control by grain contacts 599(Fig. 1), we derive a general expression for the magnitude of the 600 Lyapunov exponent in random granular media as a function of the coordination number z_c , the solid volume fraction ϕ , the grain diam-601 eter d and the mean pore diameter d_p . Since segment lengths must 602 double, on average, each times the segment encounters a contact, 603 that is for each distance X_c , the Lyapunov exponent can be derived 604 from equation Eq. (2) as $\lambda = d \log 2/X_c = d \log 2/(S_c/L_c)$, which requires estimating the mean segment length L_c and the mean sur-605 face area S_c swept by segments between successive contact points. 606 A geometric estimate for the mean segment length L_c is obtained 607 by assuming that an individual segment doubles its length at the 608 constant exponential rate λ until it reaches the mean pore diameter 609 d_p where it inevitably collides with a contact point located at X_c downstream, e.g. $L_c(x) = d_p/2 \exp(\log 2x/X_c)$. This expression 610 yields the average value 611

$$L_c \approx \frac{d_p}{2\log 2}.$$
 [6]
$$\begin{array}{c} 612\\ 613 \end{array}$$

From tomographic reconstruction of all the experimental runs, the average pore diameter is $d_p \approx 0.24 d$ (see Methods). Thus, we estimate $L_c \approx 0.17d$ which is in excellent agreement with the observations (Fig. 3). To develop an estimate of S_c , we consider the volume density ρ_V of contact points in the three-dimensional bead pack. As the number of grains per unit volume is $6\phi/(\pi d^3)$ and there are $z_c/2$ independent contacts per grain, the volume density of contact points is then $\rho_V = 3\phi z_c/(\pi d^3)$. Conversely, S_c is equal 620



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Fig. 6. a. Reconstruction of filament backbone (black line) from dve distribution and localisation of high curvature regions (red circles). b. Local curvature along the filament backbone (black line) with isolated cusps (red circles) and threshold value $\kappa = 10^3 d^{-1}$ for cusp detection (dashed line). Note that the end-points of filaments are considered as cusps, explaining why red circles can exist below κ . c. Exponential growth of the number (n_c) of cusps in the filament backbone as a function of the advection distance (x/d) from the injection point. The fitted exponent for n_c (grey line) is similar to that for the total filament length (dashed line), suggesting stationarity of the stretching and folding processes.

645 to the inverse of the areal density ρ_A of contact points in a filament 646 sheet. To develop a relationship between ρ_V and ρ_A , we consider a 647 series of filament sheets that arise from continuously injected line sources and extend along length Z in the cross-stream z-coordinate 648of the column, and are advected over distances X. These series of 649injection lines are also distributed along distance Y in the other 650 cross-stream *u*-direction. If we consider the average number n_V of 651contact points in the volume V = XYZ, then the number n_A of 652contact points contained within a filament sheet is $n_A = \bar{\ell}/Y n_V$, where $\bar{\ell}$ is the average span of filament sheet in the *y*-direction that 653 pass through a common contact point. The simplest estimate for $\bar{\ell}$ 654is obtained by considering the behaviour of filament sheets in a open 655laminar flow over two spheres in contact at an angle α with the 656 mean flow direction x. From symmetry arguments, the horizontal 657span $\ell(\alpha)$ is given by the projection in the plane normal to x of the contact line connecting the two sphere centres. Thus $\ell(\alpha) = d \sin \alpha$, 658and ℓ is given by the mean of $\ell(\alpha)$ over the distribution of contact 659 angles. As $\rho_V \equiv n_V/(XYZ)$ and $\rho_A \equiv n_A/(XY)$, then $\rho_A = \bar{\ell}\rho_V$. 660 For isotropic packings, contact lines are uniformly orientated in the 661 space, and α is distributed as $p(\alpha) = \sin \alpha$. Averaging over this 662 distribution then yields $\bar{\ell} \equiv d \sin \alpha = d\pi/4$. From the results above, 663 S_c for isotropic packings is then estimated as 664

$$S_c = 1/\rho_A = \frac{\pi d^3}{3\bar{\ell}\phi z_c}.$$
[7]

666 For anisotropic packings the distribution of contact orientations may 667 deviates from sin α , thus yielding different values for $\overline{\ell}$. Eq. (7) and 668 Eq. (6), provide the value of the mean fold distance $X_c = S_c/L_c$ 669 and from Eq. (2), the Lyapunov exponent reads

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671

$$\lambda = \bar{\ell} \frac{3\phi z_c d_p}{2\pi d^2}.$$
[8]

672 Using the estimates of ϕ , z_c and d_p obtained from tomographic 673 reconstruction and $\bar{\ell}/d = \pi/4 \approx 0.78$ for isotropic packings, equation 674 Eq. (8) yields $\lambda = 0.27$, a value comparable to the experimental 675 estimate ($\lambda = 0.21$). The slight overestimate of λ can be explained 676 by the anisotropy introduced by the gravitational packing of the 677 beads and the finite size of the experimental column. Indeed, 678independent measurements of $\rho_V = 2.86d^{-3}$ and of $S_c = 0.58d^2$ 679 (Fig. 3) indicate that, experimentally, $\bar{\ell}/d = (d\rho_V S_c)^{-1} \approx 0.6$, 680 instead of $\bar{\ell}/d = 0.78$ expected for isotropic packings. Using this 681 value in Eq. (8) yields $\lambda \approx 0.21$, in much better agreement with the 682 experimental estimate.

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