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▶ **To cite this version:**

Arthur Alexandre, Maxime Lavaud, Nicolas Fares, Elodie Millan, Yann Louyer, et al.. Non-Gaussian diffusion near surfaces. Physical Review Letters, 2023, 130, pp.077101. hal-03713580v3

HAL Id: hal-03713580
https://hal.science/hal-03713580v3

Submitted on 30 Nov 2022

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Non-Gaussian diffusion near surfaces

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We study the diffusion of particles confined close to a single wall and in double-wall planar channel geometries where the local diffusivities depend on the distance to the boundaries. Displacement parallel to the walls is Brownian as characterized by its variance, but it is non-Gaussian having a non-zero fourth cumulant. Establishing a link with Taylor dispersion, we calculate the fourth cumulant and the tails of the displacement distribution for general diffusivity tensors along with potentials generated by either the walls or externally, for instance gravity. Experimental and numerical studies of the motion of a colloid in the direction parallel to the wall give measured fourth cumulants which are correctly predicted by our theory. Interestingly, contrary to models of Brownian-yet-non-Gaussian diffusion, the tails of the displacement distribution are shown to be Gaussian rather than exponential. All together, our results provide additional tests and constraints for the inference of force maps and local transport properties near surfaces.

The transport properties of colloidal particles in complex media can be very different from those observed in simple fluids. In the bulk of simple fluids, beyond molecular length and time scales, the motion of a colloidal particle satisfies two important properties: (i) its Mean Squared Displacement (MSD) increases linearly with time (diffusive behavior) and (ii) the probability distribution functions (PDF) of position increments are Gaussian. In complex media, exhibiting dynamical and spatial heterogeneities, or in presence of flows or active forces, both properties (i) and (ii) are generally not satisfied. Examples range from non-Gaussian transport in hydrodynamic flows, with consequences for chemical delivery in microfluidic environments [1], to experimental observations of *anomalous* diffusion in complex fluids and biological media [2–6].

Colloidal dynamics in a large class of complex media can be described as either *Fickian-yet-non-Gaussian*, *anomalous-yet-Brownian* or *Brownian-yet-Non-Gaussian Diffusion* (BNGD).[7–12]. These terms all refer to processes with linear-in-time MSDs but non-Gaussian PDFs, usually having exponential tails. A generic explanation for this phenomenon is the *diffusing-diffusivity* mechanism Ref. [13]. In this scenario, BNGD is generated by a fluctuating diffusion constant, arising for example from fluctuations of the local density or of the gyration radius of complex macromolecules [14]. The diffusing-diffusivity mechanism has been further explored [15–23], but in most studies the assumptions invoked for the dynamically evolving diffusivity are generic but rather phenomenological. To the best of our knowledge, with the exception of the Brownian motion of an ellipsoidal particle [24–26], there is currently no experimental realization of a system exhibiting *fluctuating diffusivity* at all times where the local diffusivity is quantified both experimentally, numerically and theoretically over broad spatial and temporal ranges.

In this Letter, we study the non-Gaussian diffusive motion of a colloidal particle near a hard wall. Hydrodynamic interactions at walls strongly modify the stochastic motion of neighboring objects [27–33]. The local diffusivity parallel to the wall depends on the distance to the wall which itself fluctuates due to diffusion perpendicular to the wall, thus generating the diffusing-diffusivity mechanism. Note that a similar situation was previously considered in Ref. [34], but that study mainly focused on the motion perpendicular to the wall: in this case, the non-Gaussian behavior due to diffusing diffusivity can be observed only at small times, since at long times the presence of an interaction potential with the wall induces non-Gaussian displacements – even for uniform diffusivity. Furthermore, the non-Gaussianity of the motion in the parallel direction could not be resolved in Ref [34]. Here, we focus on the motion parallel to the wall which is a genuine realization of diffusing diffusivity at all times. Our theoretical analysis identifies a formal link with Taylor dispersion. In particular, we provide a calculation, that we verify experimentally and numerically, of the fourth cumulant of the displacement along the walls, which quantifies non-Gaussianity at all times. We also show that the tails of the PDF are Gaussian rather than exponential.

Physical model. We consider a Brownian particle of radius a that is confined between two walls separated by a distance $2H_\mathrm{p}$, as shown in Fig. 1. The particle diffuses along the channel (*i.e.* the x-axis) and perpendicularly to it (*i.e.* the z-axis) with respective height-dependent diffusion coefficients $D_\parallel(z)$ and $D_\perp(z)$, and is subject to a potential $V(z)$. The probability density $p(z,t)$ about z at time t thus obeys the Fokker-Planck equation $\partial_t p =$

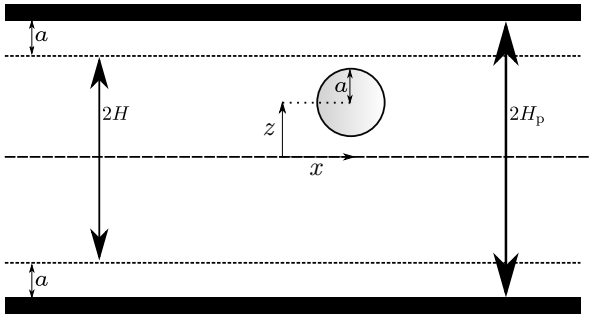


FIG. 1. Schematic: a particle of radius a diffuses in two dimensions, between two walls separated by a distance $2H_{\rm p}$.

$-\mathcal{H}p(z,t)$, where

$$\mathcal{H}\cdot = -\frac{\partial}{\partial z}\left\{D_\perp(z)\left[\frac{\partial}{\partial z}\cdot + \beta\frac{\partial V(z)}{\partial z}\cdot\right]\right\} , \qquad (1)$$

with $\beta = 1/(k_{\rm B}T)$, where $k_{\rm B}$ is Boltzmann's constant and T is the temperature. We assume no-flux conditions at the walls. In the long-time limit, the system equilibrates along the z direction and attains a Gibbs-Boltzmann distribution (see Fig. 2(a)):

$$p_0(z) = \frac{e^{-\beta V(z)}}{\int_{-H}^{H} e^{-\beta V(z')}dz'} . \qquad (2)$$

We denote by $Z_t \in [-H, H]$ the height of the center of the particle, $H = H_{\rm p} - a$ the effective channel height available to the particle, and X_t the position of the center of the particle along the channel. The second and fourth cumulants

$$\langle X_t^2\rangle_{\rm c} \equiv \langle X_t^2\rangle, \qquad \langle X_t^4\rangle_{\rm c} \equiv \langle X_t^4\rangle - 3\langle X_t^2\rangle^2 , \qquad (3)$$

characterize the transport properties of the particle. Here, $\langle\cdot\rangle$ denotes the ensemble average, and the initial condition is $X_{t=0} = 0$, while $Z_{t=0}$ follows the equilibrium distribution p_0. Note that $\langle X_t^4\rangle_{\rm c}$ vanishes if X_t is Gaussian, therefore its evaluation is the simplest way to quantify the non-Gaussian nature of the process X_t. We also define the related non-Gaussianity parameter $\alpha(t) \equiv \langle X_t^4\rangle_{\rm c}/\langle X_t^2\rangle_{\rm c}^2$.

General theory. The process X_t obeys the stochastic differential equation:

$$dX_t = \sqrt{2D_\parallel(Z_t)}dB_{x,t} , \qquad (4)$$

where the Gaussian increments $dB_{x,t}$ have $\langle dB_{x,t}\rangle = 0$ and $\langle dB_{x,t}^2\rangle = dt$. In Eq. (4), we use the Ito prescription of the stochastic calculus, however $D_\parallel(Z_t)$ is independent of X_t and so this choice is unimportant. Integrating Eq. (4) gives

$$X_t = \int_0^t \sqrt{2D_\parallel(Z_\tau)}dB_{x,\tau} . \qquad (5)$$

Squaring this and using the independence of $dB_{x,t}$ and Z_t, then taking the average yields

$$\langle X_t^2\rangle_{\rm c} \equiv \langle X_t^2\rangle = 2t\int_{-H}^{H} dz\, D_\parallel(z)p_0(z) = 2\left\langle D_\parallel\right\rangle_0 t , \qquad (6)$$

where $\langle\cdot\rangle_0$ denotes the average with respect to the equilibrium distribution $p_0(z)$. The MSD is purely linear in time, so that X_t is Brownian at all times.

Taking the fourth-power of Eq. (5) and using Wick's (or Isserlis') theorem [38] gives [39]

$$\frac{\langle X_t^4\rangle_{\rm c}}{12} = \int_0^t ds\int_0^t ds'[\langle D_\parallel(Z_s)D_\parallel(Z_{s'})\rangle - \langle D_\parallel\rangle_0^2]. \qquad (7)$$

Here, we draw an analogy with Taylor dispersion, for the dispersion of particles in channels in presence of hydrodynamic flows. We imagine the same process Z_t, but consider the convective displacement given along the channel by $Y_t = \int_0^t ds\ u(Z_s)$, where $u(z)$ is an arbitrary imposed flow field along the channel. The first two cumulants of Y_t in this problem are

$$\begin{aligned}\langle Y_t\rangle_{\rm c} &= \langle u\rangle_0 t,\\ \langle Y_t^2\rangle_{\rm c} &= \int_0^t ds\int_0^t ds'\ [\langle u(Z_s)u(Z_{s'})\rangle - \langle u\rangle_0^2].\end{aligned} \qquad (8)$$

Comparing the above expressions with Eqs. (6) and (7) we see that the second and fourth cumulants of X_t are proportional to the average and the variance of Y_t in a Taylor dispersion problem with the formal correspondence $u(z) = D_\parallel(z)$. Taylor dispersion has been widely studied [40–52], and we can exploit existing results for the MSD at all times from Ref. [52], yielding the explicit expression:

$$\begin{aligned}\langle X_t^4\rangle_{\rm c} = 24\int_{-H}^{H} dz\int_{-H}^{H} dz'\, D_\parallel(z)D_\parallel(z')p_0(z')\\ \times\sum_{\lambda>0}\left[\frac{t}{\lambda} - \frac{1-e^{-\lambda t}}{\lambda^2}\right]\psi_{{\rm R}\lambda}(z)\psi_{{\rm L}\lambda}(z') ,\end{aligned} \qquad (9)$$

where $\psi_{{\rm R}\lambda}(z)$ and $\psi_{{\rm L}\lambda}(z)$ respectively denote the right and left eigenfunctions of $\mathcal{H}$, with eigenvalue λ, and the normalization $\int_{-H}^{H} dz\ \psi_{{\rm L}\lambda}(z)\psi_{{\rm R}\lambda}(z) = 1$. In practice, this general expression can be evaluated by numerically computing the eigenfunctions after discretizing the operator $\mathcal{H}$. This formula simplifies at short times into (see SI [39]):

$$\left\langle X_t^4\right\rangle_{\rm c} \underset{t\to 0}{\simeq} 12\,t^2\left[\left\langle D_\parallel^2\right\rangle_0 - \left\langle D_\parallel\right\rangle_0^2\right] . \qquad (10)$$

We see that the initial non-Gaussianity parameter $\alpha(t = 0)$ is finite and is proportional to the variance of $D_\parallel(z)$ with respect to the equilibrium distribution, as in Ref. [13]. The late-time behavior is (see SI [39])

$$\langle X_t^4\rangle_{\rm c} \underset{t\to+\infty}{\simeq} 24\,(D_4 t - C_4) , \qquad (11)$$

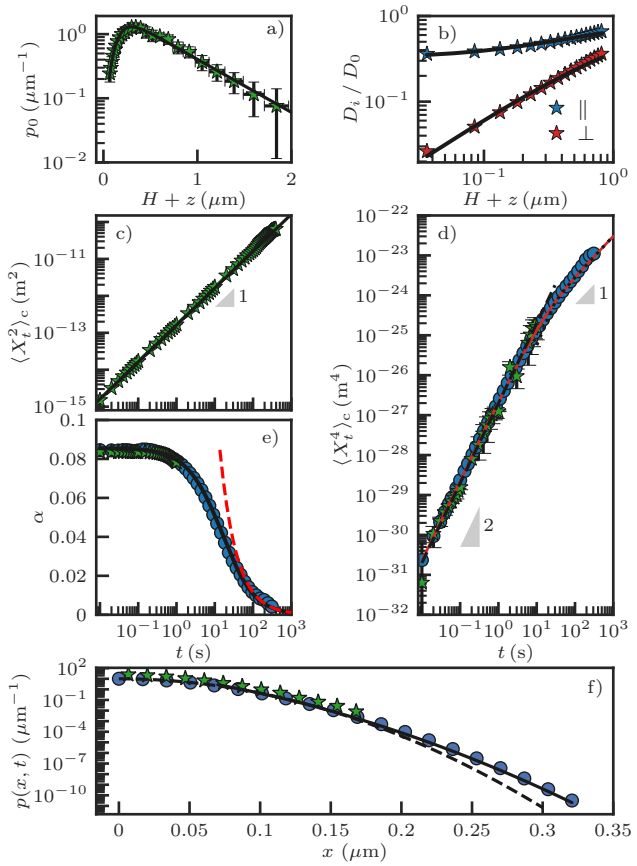


FIG. 2. (a) Experimental long-time PDF p_0 for position z, as a function of the distance $H + z$ to the bottom wall. Solid lines show the best fit to the Gibbs-Boltzmann distribution of Eq. (2), using $V(z)$ in Eq. (16), with $B = 5.0$, $l_D = 88$ nm and $l_B = 526$ nm at room temperature. Here, $H_p = 40$ μm. Error bars give 95% confidence intervals. (b) Experimentally-measured horizontal ($i = \parallel$) and vertical ($i = \perp$) local diffusion coefficients $D_i(z)$, normalized by the bulk value D_0. Solid lines are theoretical predictions $D_i(z)$ using Eqs. (17) and (18). (c) Experimentally-measured second cumulant $\langle X_t^2 \rangle_c$. The solid line corresponds to Eq. (6), with $\langle D_\parallel \rangle_0 = 0.58\, D_0$. The slope triangle indicates an exponent 1. (d) Experimentally-measured (green stars) and numerically-simulated (blue dots) fourth cumulant $\langle X_t^4 \rangle_c$. The red solid line represents the prediction of Eq. (9), while the black dashed and dotted lines are its short-time and long-time asymptotics of Eqs. (10) and (11), with no adjustable parameter. The slope triangles indicate exponents 2 and 1. (e) Non-Gaussianity parameter $\alpha \equiv \langle X_t^4 \rangle_c / \langle X_t^2 \rangle_c^2$ as a function of time t, computed from the data and theoretical predictions in (c) and (d). The red dashed line shows the predicted $\sim 1/t$ decay (see SI [39]). (f) PDF in horizontal displacement, at time increment $t = 0.01$ s, from experiments (green stars) and numerical simulations (blue dots). The Gaussian tail predicted in Eq. (S45) (see SI [39]) is also shown (solid line), as well as a simple Gaussian distribution (dashed line) with the proper mean and variance of the data.

where the explicit expression of C_4 is given in the Supplementary Information (SI) [39], and where:

$$D_4 = \left\langle \frac{\left[J(z) e^{\beta V(z)}\right]^2}{D_\perp(z)} \right\rangle_0 , \tag{12}$$

with:

$$J(z) = \int_{-H}^{z} dz' e^{-\beta V(z')} \left[D_\parallel(z') - \langle D_\parallel \rangle_0 \right] . \tag{13}$$

From the above we see that the non-Gaussianity parameter satisfies $\alpha(t) \propto 1/t$, for large t.

Analytic strong confinement theory. We consider the case of a narrow channel where we approximate the local diffusion coefficients by the quadratic expressions [39, 53, 54]:

$$D_\perp(z) \approx D_{\perp 0} \left(1 - \frac{z^2}{H^2}\right), \; D_\parallel(z) \approx D_{\parallel 0} \left(1 - \frac{z^2}{H_s^2}\right), \tag{14}$$

where H_s is a characteristic distance that can be considered as a slip-like length if $H_s > H$. The coefficients $D_{\perp 0}$ and $D_{\parallel 0}$ depend on the effective channel height H and on the particle radius a. In principle, the no-slip boundary condition must impose that $D_\parallel(z)$ is zero at the walls, which would imply that $H_s = H$. However, numerically, $D_\parallel(z)$ is found to be quadratic near the channel center and decays rapidly to zero near the walls [39, 54]. Here, Eq. (9) can be evaluated by noting that the eigenfunctions are the Legendre polynomials $P_n(z/H)$ of degree n, leading to:

$$\frac{\langle X_t^4 \rangle_c}{24} = \frac{2 D_{\parallel 0}^2 H^6 t}{135 D_{\perp 0} H_s^4} - \frac{D_{\parallel 0}^2 H^8 \left[1 - e^{-\frac{6 D_{\perp 0} t}{H^2}}\right]}{405 D_{\perp 0}^2 H_s^4} . \tag{15}$$

In this model, there is only one relaxation time, equal to the time for the particle to diffuse perpendicularly. This result can be generalized to arbitrary $D_\parallel(z)$, keeping the same form of $D_\perp$, in which case many relaxation times appear (see SI [39]). The non-Gaussianity is such that $\alpha(0) = (12H^4)/(5(3H_s^2 - H^2)^2)$ and is thus of order one. At short times, if one takes $H_s = H$ then $\alpha(0) = 3/5$.

Experimental system. A polystyrene bead, with radius $a = 1.519 \pm 0.009$ μm diffuses in an aqueous NaCl solution confined between two glass walls. Its trajectory is tracked in three dimensions using Mie holography [37]. Here, $H_p = 40$ μm, so that $H_p \gg a$. The density mismatch of the particle is chosen such that the particle is visibly localized near the lower wall due to gravity (see Fig. 2(a)). So, the effect of the upper wall is negligible both in terms of hydrodynamic and conservative forces. The bead is submitted to a potential:

$$\beta V(z) = B\, e^{-\frac{H+z}{l_D}} + B\, e^{-\frac{H-z}{l_D}} + \frac{z}{l_B} . \tag{16}$$

The first two terms of the right-hand side are the screened electrostatic interactions between the negatively-charged

surfaces of the walls and the bead, as given mean-field theory [55], where $l_{\rm D}$ is the Debye length and B is a dimensionless number depending in particular on the wall and bead surface charges. We have used the superposition approximation, valid for gaps large compared to $l_{\rm D}$ so that the two potentials can be simply summed. The third term accounts for gravity: $l_{\rm B} = k_{\rm B}T/(\frac{4}{3}\pi a^3 \Delta\rho g)$ is the Boltzmann length, with g the gravitational acceleration, and $\Delta\rho$ the density mismatch between the polystyrene bead and the solution. Equations (2) and (16) are used to fit the experimentally measured equilibrium distribution $p_0(z)$. The agreement is good with $B = 5.0 \pm 0.3$, $l_{\rm D} = 88 \pm 2$ nm and $l_{\rm B} = 526 \pm 5$ nm, as shown in Fig. 2(a). Assuming a perfect sphere, the value of $l_{\rm B}$ gives a density mismatch $\Delta\rho = 53$ kg/m^3, which is within 5% error of the tabulated value of 50 kg/m^3.

Moving on to hydrodynamic interactions, $D_\parallel$ and $D_\perp$ are inferred from the experimentally observed trajectories [37, 39] and are shown in Fig. 2(b). The results agree with the Stokes-Einstein relations $D_i(z) = k_{\rm B}T/[6\pi a \mu_i(z)]$, where $i \in \{\parallel, \perp\}$ and where μ_i are the components of the effective viscosity tensor [56]. The transverse component reads [57]:

$$\mu_\parallel(z) = \mu_0 \left(1 - \frac{9}{16}\zeta + \frac{1}{8}\zeta^3 - \frac{45}{256}\zeta^4 - \frac{1}{16}\zeta^5\right)^{-1}, \quad (17)$$

with $\zeta = a/(z + H_{\rm p})$, and where μ_0 is the bulk viscosity. The normal component was derived in Ref. [56] as an infinite sum, which can be Padé-approximated to within 1% numerical accuracy by [58]

$$\mu_\perp(z) = \mu_0 \, \frac{6\,(z+H)^2 + 9a\,(z+H) + 2a^2}{6\,(z+H)^2 + 2a\,(z+H)} \, . \quad (18)$$

These expressions, through the associated diffusion coefficients, are in agreement with the experimental data at room temperature and with $\mu_0 = 1$ mPa.s for water, as shown in Fig. 2(b). Combined with the previously-mentioned equilibrium properties (see Eq. (16)), they can thus be used as inputs to compute the theoretical values of the fourth cumulant of X_t.

Comparison with theory. Experimentally, the displacements X_t are used to estimate $\langle X_t^2\rangle_{\rm c}$ and $\langle X_t^4\rangle_{\rm c}$, computed using the method of sliding averages described in SI [39] and leading to Figs. 2(c,d). First, the effective diffusion constant, $\langle D_\parallel\rangle_0$ defined in Eq. (6), is given numerically by $\langle D_\parallel\rangle_0 = 0.58\, D_0$, where $D_0 = k_{\rm B}T/(6\pi a\mu_0)$ is the bulk diffusion constant. This is in agreement with the experimental data shown in Fig. 2(c). Secondly, the short-time theoretical prediction in Eq. (10) correctly predicts the experimental data for $\langle X_t^4\rangle_{\rm c}$, with no adjustable parameter (see Fig. 2(d)). Lack of data at long times makes it difficult to check the late-time prediction given by Eq. (11). This result can however be verified through numerical simulations, as shown in Fig. 2(d), where the simulation details are given in SI [39]. The whole range of experimental and numerical data can be reproduced, up to error bars, by the exact prediction of Eq. (9), where the eigenfunctions and eigenvalues of $\mathcal{H}$ are computed numerically. We thus have a well-controlled experimental system with a MSD that is linear in time, at all times, as well as non-Gaussian statistics.

Distribution of displacements. We now study the PDF $p(x,t)$ of the displacement x at time t, in order to determine in particular whether or not it displays apparent exponential tails, as often observed in BNGD [7, 8, 12, 15, 22, 59–63] and other contexts [64]. We consider a class of systems bounded in the z direction, with a single maximum in $D_{||}(z)$, as is the case in our simulations, experiments and the simple channel model. First, at short times, it is well known [13, 15, 24, 37] that

$$p(x,t) \simeq \int_{-H}^{H} dz \; p_0(z) \; \frac{e^{-x^2/[4D_\parallel(z)t]}}{\sqrt{4\pi D_\parallel(z) t}} \, . \quad (19)$$

An analysis of this expression shows that, for large x, one has $p(x,t) \simeq A e^{-x^2/4D_{||}(z^*)t}$, where z^* is the point where $D_{||}(z)$ is maximal. In SI [39], we compute A, and we show in Fig. 2(f) that such a Gaussian tail is quantitatively recovered in the numerical simulations and experiments.

At late times, the PDF can be analysed using its moment-generating function $g(q,t) = \langle e^{qX_t}\rangle$, which reads:

$$g(q,t) = \left\langle e^{q\int_0^t dB_{x,s}\sqrt{2D_\parallel(Z_s)}} \right\rangle = \left\langle e^{q^2\int_0^t ds D_\parallel(Z_s)} \right\rangle \, , \quad (20)$$

where the last equality is obtained by averaging over the Gaussian noise $dB_{x,s}$. Interestingly, $g(q,t) = \langle e^{q^2 Y_t}\rangle$ is related to the moment-generating function for the above-mentioned Taylor dispersion problem. We can thus use the tools introduced in the context of Taylor dispersion [65–67] to obtain the extreme tails of $p(x,t)$ at long times, with $p(x,t) \sim e^{-tf(x/t)}$. By extreme tails, we mean that $\xi = x/t$ is $\mathcal{O}(1)$, thus far from the diffusive scaling limit at late times where $x/\sqrt{t}$ is $\mathcal{O}(1)$. In SI [39], we show that for large ξ,

$$f(\xi) = \frac{1}{4D_{||}(z^*)} \left[\xi + \mathrm{sgn}(\xi)\sqrt{\frac{|D''_{||}(z^*)|D_\perp(z^*)}{2}}\right]^2 \, . \quad (21)$$

The paths contributing to $f(\xi)$ in this regime stay close to the region of maximal diffusivity, but they are rare and are exponentially suppressed with respect to paths which scale diffusively.

The presence of Gaussian tails is thus generic for the class of problems studied here, and the exponential tails seen in other diffusing-diffusivity models [13] are absent. The fact that $D_\parallel(z)$ has a maximal value is the main difference between our system and those considered in Ref. [13], where the diffusion constant is unbounded. In

fact, it was already noted in Ref. [13] that the PDF tails are generally not strictly exponential, depending on the local diffusivity distribution. The Gaussian tails in our system contrast with the case of Continuous Time Random Walks [68], and diffusion in confined disordered media [12, 61, 62] or glassy [59, 60] systems, where exponentials tails are present. These situations tend to involve trapping, hoping or caging mechanisms (possibly due to heterogeneities) which are absent in our system.

The late-time corrections to Gaussianity in the diffusive-scaling region are dominated by the fourth-order cumulant, which gives a correction to the PDF that decays as $\sim 1/t$ (see SI [39]). Finally, replacing $q = -ik$ in Eq. (20) gives the Fourier transform $\hat{p}(k,t) = \int_{-\infty}^{\infty} dx\ e^{-ikx} p(x,t)$. This can be computed numerically (see SI [39]). Taking the inverse Fourier transform gives a numerical evaluation of $p(x,t)$ in good agreement with the numerical and experimental PDFs (see Fig. S2 in SI [39]). We have also examined the case where the channel width is much smaller ($H_\mathrm{p} = 5.5\,\mu$m). Similar effects are seen, but the asymptotic regime of linear temporal growth of the fourth cumulant is attained much more quickly.

Conclusion. We have addressed a physical realization of diffusing-diffusivity motion based on confined colloids by establishing a mapping onto Taylor dispersion, where the diffusivity formally corresponds to a flow field. This analogy gives quantitative predictions for the diffusion along the channel, which agree with experimental and numerical data with no additional fitting parameter apart from the physical ones obtained independently in the experiments. We have also shown that the tails of the PDF are not exponential but modified Gaussian in this generic class of models, both at short and long times. One should note that the effective diffusion constant along the channel only depends on the equilibrium properties of the process normal to the wall, and is otherwise independent of its dynamics. The fourth cumulant however depends on the precise details of the dynamics via the two-point probability density functions. The fourth cumulant thus carries extra information on the dynamics, and, as such, appears to be a key statistical observable that can further contribute to improve the experimental resolution for the inference of force maps and local transport properties in heterogeneous environments [35, 36] and near surfaces [37].

Acknowledgments: The authors thank Joshua McGraw and Maxence Arutkin for interesting discussions. They acknowledge financial support from the European Union through the European Research Council under EMetBrown (ERC-CoG-101039103) grant. Views and opinions expressed are however those of the authors only and do not necessarily reflect those of the European Union or the European Research Council. Neither the European Union nor the granting authority can be held responsible for them. The authors also acknowledge financial support from the Agence Nationale de la Recherche under EMetBrown (ANR-21-ERCC-0010-01), Softer (ANR-21-CE06-0029), Fricolas (ANR-21-CE06-0039), and ComplexEncounters (ANR-21-CE30-0020) grants. Finally, they thank the Soft Matter Collaborative Research Unit, Frontier Research Center for Advanced Material and Life Science, Faculty of Advanced Life Science at Hokkaido University, Sapporo, Japan.

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