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),\textsuperscript{[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 \( 2H \), as shown in Fig. 1. The particle diffuses along the channel (\textit{i.e.} the \( x \)-axis) and perpendicularly to it (\textit{i.e.} the \( z \)-axis) with respective height-dependent diffusion coefficients \( D_x(z) \) 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 $2H_p$.

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

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

with $\beta = 1/(k_B T)$, where $k_B$ 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)):

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

We denote by $Z_t \in [-H,H]$ the height of the center of the particle, $H = H_p - a$ 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

$$\langle X_t^2 \rangle_c \equiv \langle X_t^2 \rangle, \quad \langle X_t^4 \rangle_c \equiv \langle X_t^4 \rangle - 3\langle X_t^2 \rangle^2, \quad (3)$$

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 $\langle X_t^4 \rangle_c$ 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 $\alpha(t) \equiv \langle X_t^4 \rangle_c/\langle X_t^2 \rangle^2$.

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

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

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

$$X_t = \int_0^t \sqrt{2D_\parallel(Z_r)} dB_{x,r}. \quad (5)$$

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

$$\langle X_t^2 \rangle_c \equiv \langle X_t^2 \rangle = 2t \int_{-H}^{H} dz D_\parallel(z) p_0(z) = 2 \langle D_\parallel \rangle_0 t, \quad (6)$$

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]

$$\frac{\langle X_t^4 \rangle_c}{12} = \int_0^t dt \int_0^t ds [\langle D_\parallel \rangle(Z_s D_\parallel(Z_s)) - \langle D_\parallel \rangle_0^2]. \quad (7)$$

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 $Y_t$, 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

$$\langle Y_t \rangle_c = \langle u \rangle_0 t, \quad \langle Y_t^2 \rangle_c = \int_0^t dt \int_0^t ds' [\langle u(Z_s) u(Z_s') \rangle - \langle u \rangle_0^2]. \quad (8)$$

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:

$$\langle X_t^4 \rangle_c = 24 \int_{-H}^{H} dz \int_{-H}^{H} dz' D_\parallel(z) D_\parallel(z') p_0(z') \times \sum_{\lambda>0} \left[ t - \frac{1 - e^{-\lambda t}}{\lambda^2} \right] \psi_{R\lambda}(z) \psi_{\lambda}(z'), \quad (9)$$

where $\psi_{R\lambda}(z)$ and $\psi_{\lambda}(z)$ respectively denote the right and left eigenfunctions of $\mathcal{H}$, with eigenvalue $\lambda$, and the normalization $\int_{-H}^{H} dz \psi_{R\lambda}(z) \psi_{\lambda}(z) = 1$. 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]):

$$\langle X_t^4 \rangle_c \sim \int_0^t \frac{12 t^2}{\langle D_\parallel \rangle_0^2} \left[ \langle D_\parallel \rangle_0^2 - \langle D_\parallel \rangle_0^2 \right]. \quad (10)$$

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])

$$\langle X_t^4 \rangle_c \sim \frac{24}{t \rightarrow \infty} \left( D_4 t - C_4 \right), \quad (11)$$
The first two terms of the right-hand side are the screened electrostatic interactions between the negatively-charged particles. The slope triangles indicate exponents 2 and 1. (e) Experimentally-measured second cumulant $\langle X^2_t \rangle$. The solid line corresponds to Eq. (6), with $\langle D_{||0} \rangle = 0.58 D_0$. The non-Gaussianity parameter $\alpha$ is such that $\alpha(0) = (12H^4)/(5(3H^2 s - H^2)^2)$ 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 $a = 1.519 \pm 0.009 \mu m$ diffuses in an aqueous NaCl solution confined between two glass walls. Its trajectory is tracked in three dimensions using Mie holography [37]. Here, $H_p = 40 \mu m$, 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:

$$\beta V(z) = B e^{-\frac{H_s}{H_p}} + B e^{-\frac{H_s}{H_s}} + \frac{z}{l_B}.$$  \hspace{1cm} (16)
surfaces of the walls and the bead, as given mean-field theory [55], where \( l_D \) 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 \( l_D \) so that the two potentials can be simply summed. The third term accounts for gravity: \( l_B = k_B T/(4\pi \eta a^3 \Delta \rho g) \) 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 \( B = 5.0 \pm 0.3 \), \( l_D = 88 \pm 2 \) nm and \( l_B = 526 \pm 5 \) nm, as shown in Fig. 2(a). Assuming a perfect sphere, the value of \( l_D \) 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 \( D_i(z) = k_B T/(6\pi a \mu_i(z)) \), where \( i \in \{\parallel, \perp\} \) and where \( \mu_i \) are the components of the effective viscosity tensor [56]. The transverse component reads [57]:

\[
\mu_\perp(z) = \mu_0 \left( 1 - \frac{9}{16} \zeta + \frac{5}{8} \zeta^3 - \frac{45}{256} \zeta^4 - \frac{1}{16} \zeta^5 \right)^{-1},
\]

(17)

with \( \zeta = a/(z + H_p) \), and where \( \mu_0 \) 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]

\[
\mu_\parallel(z) = \mu_0 \frac{6(z + H)^2 + 9a(z + H) + 2a^2}{6(z + H)^2 + 2a(z + H)}. \tag{18}
\]

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 \( \langle X_t^2 \rangle_c \) and \( \langle X_t^4 \rangle_c \), 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 \( D_0 = k_B T/(6\pi a \mu_0) \) 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 \( \langle X_t^4 \rangle_c \), 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 \( H \) 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 \( D_\parallel(z) \), 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

\[
p(x,t) \simeq \int_{-H}^{H} dz \ p_0(z) \ e^{-x^2/[4D_\parallel(z)t]} \frac{1}{\sqrt{4\pi D_\parallel(z)t}}. \tag{19}
\]

An analysis of this expression shows that, for large \( x \), one has \( p(x,t) \sim A e^{-x^2/[4D_\parallel(z)t]} \), where \( z^* \) is the point where \( D_\parallel(z) \) 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:

\[
g(q,t) = \langle e^{q \int_0^t dB_{zs}} \sqrt{4D_\parallel(Z_s)} \rangle = \left< e^{q^2 \int_0^t ds D_\parallel(z_s)} \right>, \tag{20}
\]

where the last equality is obtained by averaging over the Gaussian noise \( dB_{zs} \). 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 \( p(x,t) \sim e^{-f(x)/t} \). By extreme tails, we mean that \( \xi = x/t \) is \( O(1) \), thus far from the diffusive scaling limit at late times where \( x/\sqrt{t} \) is \( O(1) \). In SI [39], we show that for large \( \xi \),

\[
f(\xi) = \frac{1}{4D_\parallel(z^*)} \left[ \xi + \text{sgn}(\xi) \sqrt{\frac{D_\parallel(z^*) D_\perp(z^*)}{2}} \right]^2. \tag{21}
\]

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.
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 $\tilde{p}(k, t) = \int_{-\infty}^{\infty} dx \ e^{-ikx}p(x, t)$. 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 ($H_p = 5.5 \mu$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].

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tics to subordination of diffusing diffusivities. *Phys. Rev. X* **7**, 021002 (2017).

[16] Sposini, V., Chechkin, A. & Metzler, R. First passage statistics for diffusing diffusivity. *J. Phys. A: Math Theor* **52**, 04LT01 (2018).

[17] Lanoiselée, Y., Moutal, N. & Grebenkov, D. S. Diffusion-limited reactions in dynamic heterogeneous media. *Nat. Comm.* **9**, 4398 (2018).

[18] Lanoiselée, Y. & Grebenkov, D. S. A model of non-gaussian diffusion in heterogeneous media. *J. Phys. A: Math. Theor.* **51**, 145602 (2018).

[19] Jain, R. & Sebastian, K. L. Diffusion in a crowded, rearranging environment. *J. Phys. Chem. B* **120**, 3988–3992 (2016).

[20] Jain, R. & Sebastian, K. L. Diffusing diffusivity: survival in a crowded rearranging and bounded domain. *J. Phys. Chem. B* **120**, 9215–9222 (2016).

[21] Yin, Q., Li, Y., Marchesoni, F., Nayak, S. & Ghosh, P. K. Non-gaussian normal diffusion in low dimensional systems. *Frontiers of Physics* **16**, 1–14 (2021).

[22] Miotto, J. M., Pigolotti, S., Chechkin, A. V. & Roldán, V. Effects of hydrodynamic interactions on the near-surface diffusion of spheroidal molecules. *ACS omega* **4**, 17016–17030 (2019).

[23] Felderhof, B. Effect of the wall on the velocity autocorrelation function and long-time tail of brownian motion. *J. Phys. Chem. B* **109**, 21406–21412 (2005).

[24] Munk, T., Höfling, F., Frey, E. & Franosch, T. Effective perren theory for the anisotropic diffusion of a strongly hindered rod. *EPL (Europhysics Letters)* **85**, 30003 (2009).

[25] Czajka, P., Antosiewicz, J. M. & Dlugosz, M. Effects of hydrodynamic interactions on the near-surface diffusion of spheroidal molecules. *ACS omega* **4**, 17016–17030 (2019).

[26] Huang, K. & Szlufarska, I. Effect of interfaces on the nearby brownian motion. *Nat. Comm.* **6**, 1–6 (2015).

[27] Choudhury, U., Straube, A. V., Fischer, P., Gibbs, J. G. & Höfling, F. Active colloidal propulsion over a crystalline surface. *New J. Phys.* **19**, 125010 (2017).

[28] Hertlein, C., Helden, L., Gambassi, A., Dietrich, S. & Bechinger, C. Direct measurement of critical casimir forces. *Nature* **451**, 172–175 (2008).

[29] Helden, L., Eichhorn, R. & Bechinger, C. Direct measurement of thermophoretic forces. *Soft Matt.* **11**, 2379–2386 (2015).

[30] Mats, M., Chubynsky, M. V. & Bechhoefer, J. Test of the diffusing-diffusivity mechanism using near-wall colloidal dynamics. *Phys. Rev. E* **96**, 042604 (2017).

[31] Serov, A. S. et al. Statistical tests for force inference in heterogeneous environments. *Scientific Reports* **10**, 1–12 (2020).

[32] Frishman, A. & Ronceray, P. Learning force fields from stochastic trajectories. *Phys. Rev. X* **10**, 021009 (2020).

[33] Lavaud, M., Salez, T., Louyer, Y. & Amarouchene, Y. Stochastic inference of surface-induced effects using brownian motion. *Phys. Rev. Res.* **L032011** (2021). Publisher: APS.

[34] Coffey, W. & Kalmykov, Y. P. The Langevin equation: with applications to stochastic problems in physics, chemistry and electrical engineering, vol. 27 (World Scientific, 2012).

[35] See Supplemental Material at [URL will be inserted by publisher] for further experimental, numerical and analytical details, where we also cite Refs. [69–73].

[36] Barton, N. On the method of moments for solute dispersion. *J. Fluid. Mech.* **126**, 205–218 (1983).

[37] Biswas, R. R. & Sen, P. N. Taylor dispersion with absorbing boundaries: A stochastic approach. *Phys. Rev. Lett.* **98**, 164501 (2007).

[38] Vedel, S., Hovad, E. & Bruus, H. Time-dependent thermal dispersion of an initial point concentration. *J. Fluid. Mech.* **752**, 107–122 (2014).

[39] Li, Z. et al. Near-wall nanoveloctimetry based on total internal reflection fluorescence with continuous tracking. *Journal of Fluid Mechanics* **766**, 147–171 (2015).

[40] Guérit, T. & Dean, D. S. Force-induced dispersion in heterogeneous media. *Phys. Rev. Lett.* **115**, 020601 (2015).

[41] Guérit, T. & Dean, D. S. Kubo formulas for dispersion in heterogeneous periodic nonequilibrium systems. *Phys. Rev. E* **92**, 062103 (2015).

[42] Vilquin, A. et al. Time dependence of advection-diffusion coupling for nanoparticle ensembles. *Phys. Rev. Fluids* **6**, 064201 (2021).

[43] Brenner, H. & Edwards, D. A. *Macrotransport Processes* (Butterworth-Heinemann, 1993).

[44] Hidalgo-Soria, M. & Grebenkov, D. S. Diffusion analytics for spheroidal molecules. *Phys. Rev. Lett.* **102**, 012109 (2020).

[45] Alexandre, A., Guérit, T. & Dean, D. S. Generalized Taylor dispersion of an initial point concentration. *Soft Matt.* **3**, 1–6 (2021).

[46] Elgeti, J., Winkler, R. G. & Gompper, G. Physics of microswimmers—single particle motion and collective behavior: a review. *Rep. Progr. Phys.* **78**, 056601 (2015).

[47] Jeney, S., Lukić, B., Kraus, J. A., Franosch, T. & Forró, L. Anisotropic memory effects in confined colloidal diffusion. *Phys. Rev. Lett.* **100**, 240604 (2008).

[48] Israelachvili, J. N. *Intermolecular and surface forces, second edition* (Academic press, London, 1991).

[49] Alexandre, A., Guérit, T. & Dean, D. S. Generalized Taylor dispersion for translationally invariant microfluidic systems. *Phys. Fluids* **33**, 082004 (2021).

[50] Balakotaiah, V., Chang, H.-c. & Smith, F. Dispersion of chemical solutes in chromatographs and reactors. *Philosophical Transactions of the Royal Society of London. Series A: Physical and Engineering Sciences* **351**, 39–75 (1995).

[51] Watt, S. D. & Roberts, A. J. The accurate dynamic modelling of contaminant dispersion in channels. *SIAM J. Appl. Math.* **55**, 1016–1038 (1995).

[52] Biswas, R. R. & Sen, P. N. Taylor dispersion with absorbing boundaries: A stochastic approach. *Phys. Rev. Lett.* **98**, 164501 (2007).

[53] Vedel, S., Hovad, E. & Bruus, H. Time-dependent thermal dispersion of an initial point concentration. *J. Fluid. Mech.* **752**, 107–122 (2014).

[54] Li, Z. et al. Near-wall nanoveloctimetry based on total internal reflection fluorescence with continuous tracking. *Journal of Fluid Mechanics* **766**, 147–171 (2015).

[55] Guérit, T. & Dean, D. S. Force-induced dispersion in heterogeneous media. *Phys. Rev. Lett.* **115**, 020601 (2015).

[56] Guérit, T. & Dean, D. S. Kubo formulas for dispersion in heterogeneous periodic nonequilibrium systems. *Phys. Rev. E* **92**, 062103 (2015).

[57] Vilquin, A. et al. Time dependence of advection-diffusion coupling for nanoparticle ensembles. *Phys. Rev. Fluids* **6**, 064201 (2021).

[58] Brenner, H. & Edwards, D. A. *Macrotransport Processes* (Butterworth-Heinemann, 1993).

[59] Hertlein, C., Helden, L., Gambassi, A., Dietrich, S. & Bechinger, C. Direct measurement of critical casimir forces. *Nature* **451**, 172–175 (2008).

[60] Helden, L., Eichhorn, R. & Bechinger, C. Direct measurement of thermophoretic forces. *Soft Matt.* **11**, 2379–2386 (2015).

[61] Matsu, M., Chubyhnsky, M. V. & Bechhoefer, J. Test of the diffusing-diffusivity mechanism using near-wall colloidal dynamics. *Phys. Rev. E* **96**, 042604 (2017).

[62] Serov, A. S. et al. Statistical tests for force inference in heterogeneous environments. *Scientific Reports* **10**, 1–12 (2020).

[63] Frishman, A. & Ronceray, P. Learning force fields from stochastic trajectories. *Phys. Rev. X* **10**, 021009 (2020).
loidal particles very near to a wall: Revisited. J. Chem. Phys. 113, 1228–1236 (2000).

[59] Chaudhuri, P., Berthier, L. & Kob, W. Universal nature of particle displacements close to glass and jamming transitions. Phys. Rev. Lett. 99, 060604 (2007).

[60] Rusciano, F., Pastore, R. & Greco, F. Fickian Non-Gaussian Diffusion in Glass-Forming Liquids. Phys. Rev. Lett. 128, 168001 (2022).

[61] Xue, C., Zheng, X., Chen, K., Tian, Y. & Hu, G. Probing non-Gaussianity in confined diffusion of nanoparticles. J. Phys. Chem. Lett. 7, 514-519 (2016).

[62] Xue, C., Shi, X., Tian, Y., Zheng, X., & Hu, G. Diffusion of nanoparticles with activated hopping in crowded polymer solutions. Nano Lett. 20, 3895–3904 (2020).

[63] Pastore, R., Ciarlo, A., Pesce, G., Greco, F., & Sasso, A. Rapid Fickian yet non-Gaussian diffusion after subdiffusion. Phys. Rev. Lett. 126, 158003 (2021).

[64] Silva, A. C., Prange, R. E. & Yakovenko, V. M. Exponential distribution of financial returns at mesoscopic time lags: a new stylized fact. Physica A: Statistical Mechanics and its Applications 344, 227–235 (2004).

[65] Haynes, P. & Vanneste, J. Dispersion in the large-deviation regime. part 2. cellular flow at large péclet number. J. Fluid Mech. 745, 351–377 (2014).

[66] Haynes, P. & Vanneste, J. Dispersion in the large-deviation regime. part 1: shear flows and periodic flows. J. Fluid Mech. 745, 321–350 (2014).

[67] Kahlen, M., Engel, A. & Van den Broeck, C. Large deviations in taylor dispersion. Phys. Rev. E 95, 012144 (2017).

[68] Barkai, E. & Burov, S. Packets of diffusing particles exhibit universal exponential tails. Phys. Rev. Lett. 124, 060603 (2020).

[69] Gardiner, C. W. Stochastic methods for physics, and handbook for the natural and social sciences (Springer Series in Synergetics, 2009).

[70] Øksendal, B. Stochastic differential equations (Springer, New-York, 2003).

[71] Kurzthaler, C., Leitmann, S. & Franosch, T. Intermediate scattering function of an anisotropic active brownian particle. Scientific reports 6, 1–11 (2016).

[72] Cramér, H. Mathematical methods of statistics (Princeton university press, 1946).

[73] Touchette, H. The large deviation approach to statistical mechanics. Phys. Rep. 478, 1–69 (2009).
Supplementary Information for
Non-Gaussian diffusion near surfaces
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I. THEORETICAL FORMALISM

A. Cumulants of the horizontal displacement

The fourth cumulant is obtained by direct computation:

\[
\langle X_t^4 \rangle_c = \langle X_t^4 \rangle - 3\langle X_t^2 \rangle^2 = 12 \int_0^t \int_0^t \int_0^t \int_0^t \partial_p \left[ \langle D_{\parallel}(Z_s)D_{\parallel}(Z_{s'}) \rangle - \langle D_{\parallel}(Z_s) \rangle \langle D_{\parallel}(Z_{s'}) \rangle \right], \tag{S1}
\]

where we have used Wick’s theorem. The translational invariance in the \( x \) direction means that all odd cumulants are zero. The cumulant can be rewritten as

\[
\langle X_t^4 \rangle_c = 12 \int_0^t \int_0^t \int_0^t \int_0^t \partial_p \left( \left\{ \int_0^t \int_0^t \int_0^t \int_0^t \partial_p \left[ \langle D_{\parallel}(Z_s) \rangle \langle D_{\parallel}(Z_{s'}) \rangle \right] \right\}^2 \right). \tag{S2}
\]

The latter equation has the same Kubo-type structure as the second cumulant in the Taylor dispersion problem [1]. Interestingly, from the last expression in Eq. (S2), we see that \( \langle X_t^4 \rangle_c \) takes always positive values, regardless of the expression of \( D_{\parallel}(z) \).

To proceed, we introduce the propagator \( p(z|z'; t) \), i.e. the probability to go from \( z' \) at time zero to \( z \) at time \( t \), for the process \( Z_t \). The propagator obeys:

\[
\frac{\partial p(z|z'; t)}{\partial t} = -\mathcal{H} p(z|z'; t), \tag{S3}
\]

where the operator \( \mathcal{H} \) acts on the variable \( z \), and is given by Eq. (??) of the main text, with the initial condition \( p(z|z'; 0) = \delta(z - z') \). In this framework, for the process \( X_t \), when \( Z_t \) starts from equilibrium, one has:

\[
\langle X_t^4 \rangle_c = 24 \int_0^t \int_0^t \int_0^t \int_0^t \partial_p \langle D_{\parallel}(z) \rangle \int_{-H}^H dz' D_{\parallel}(z') \int_{-H}^H dz' \langle p(z|z'; s - s') - p_0(z) \rangle p_0(z'). \tag{S4}
\]

We now introduce the left and right eigenfunctions, respectively \( \psi_{L\lambda} \) and \( \psi_{R\lambda} \), of \( \mathcal{H} \) which obey:

\[
\mathcal{H} \psi_{L\lambda} = \lambda \psi_{L\lambda}, \quad \mathcal{H} \psi_{R\lambda} = \lambda \psi_{R\lambda}, \tag{S5}
\]

with \( \lambda \) the associated eigenvalue and \( \mathcal{H}^\dagger \) the adjoint operator of \( \mathcal{H} \), which is in general not self-adjoint. The solution of Eq. (S3) for \( p(z|z'; t) \) then has the decomposition:

\[
p(z|z'; t) = \sum_{\lambda} \psi_{R\lambda}(z) \psi_{L\lambda}(z') \exp(-\lambda t). \tag{S6}
\]

The right eigenfunctions satisfy the no-flux boundary condition:

\[
\left\{ D_{\perp}(z) \left( \frac{d\psi_{R\lambda}}{dz} + \beta V'(z) \psi_{R\lambda}(z) \right) \right\}_{z=\pm H} = 0, \tag{S7}
\]

and one can show [2] that the left eigenfunctions satisfy the Neumann condition: \( \frac{d\psi_{L\lambda}(z)}{dz} \vert_{z=\pm H} = 0 \). The eigenfunctions corresponding to \( \lambda = 0 \) can be written as: \( \psi_{R0}(z) = p_0(z) \) and \( \psi_{L0}(z) = 1 \), so that they respect the normalization condition \( \int dz \psi_{R0}(z) \psi_{L0}(z) = 1 \). Using this representation of \( p(z|z'; t) \) in the Kubo formula of Eq. (S4), the fourth cumulant can be rewritten as:

\[
\langle X_t^4 \rangle_c = 24 \int_{-H}^H dz \int_{-H}^H dz' D_{\parallel}(z) D_{\parallel}(z') p_0(z') \sum_{\lambda > 0} \left[ \frac{t}{\lambda} - \frac{1}{\lambda^2} + \frac{\exp(-\lambda t)}{\lambda^2} \right] \psi_{R\lambda}(z) \psi_{L\lambda}(z'), \tag{S8}
\]
which is Eq. (??) of the main text. In principle, Eq. (S8) can be computed explicitly if the relevant eigenfunctions and eigenvalues are known, however in most cases, they are not known explicitly. Nevertheless, they can still be computed numerically using standard numerical packages and thus used to predict the full temporal behavior of $\langle X_t^4 \rangle_c$. In contrast, the short-time and long-time behaviors can be extracted analytically from Eq. (S8), as explained in the following subsection.

B. Asymptotic behavior of the fourth cumulant

In the limit where $t \to 0$, Eq. (S8) simplifies to:

$$\langle X_t^4 \rangle_c \simeq 12 t^2 \int_{-H}^{H} dz \int_{-H}^{H} dz' D_{\parallel}(z)D_{\parallel}(z')p_0(z') \sum_{\lambda > 0} \psi_{\lambda\lambda}(z)\psi_{\lambda\lambda}(z').$$

(S9)

Furthermore, the completeness relation leads to:

$$\sum_{\lambda > 0} \psi_{\lambda\lambda}(z)\psi_{\lambda\lambda}(z') = \delta(z-z') - p_0(z).$$

(S10)

Then, Eq. (S9) becomes:

$$\langle X_t^4 \rangle_c \simeq 12 t^2 \left[ \left\langle D_{\parallel}^2 \right\rangle_0 - \left\langle D_{\parallel} \right\rangle_0^2 \right].$$

(S11)

The short-time behavior of the fourth cumulant is thus quadratic in time, and is proportional to the variance of $D_{\parallel}$ with respect to the equilibrium measure.

The fourth cumulant can also be computed in the limit where $t \to \infty$, i.e. for $t \gg \lambda_1^{-1}$, where $\lambda_1$ is the first non-zero eigenvalue of $\mathcal{H}$. This is done by using a formulation in terms of Green’s functions [3, 4], which can be shown to be intimately linked to the macro-transport theory [5]. In this case, Eq. (S8) simplifies to:

$$\langle X_t^4 \rangle_c \simeq -24 (D_4 t - C_4),$$

(S12)

with

$$D_4 = \int_{-H}^{H} dz \int_{-H}^{H} dz' D_{\parallel}(z)D_{\parallel}(z')p_0(z') \sum_{\lambda > 0} \frac{\psi_{\lambda\lambda}(z)\psi_{\lambda\lambda}(z')}{\lambda},$$

(S13)

and

$$C_4 = \int_{-H}^{H} dz \int_{-H}^{H} dz' D_{\parallel}(z)D_{\parallel}(z')p_0(z') \sum_{\lambda > 0} \frac{\psi_{\lambda\lambda}(z)\psi_{\lambda\lambda}(z')}{\lambda^2}.$$  

(S14)

Using the method described in [1] (see Section III. A therein), we obtain:

$$D_4 = \left\langle \frac{\left[ J(z)e^{\beta V(z)} \right]^2}{D_\perp(z)} \right\rangle_0, \quad J(z) = \int_{-H}^{z} dz' \exp[ -\beta V(z') ] [D_\parallel(z') - \langle D_\parallel \rangle_0].$$

(S15)

This form is particularly useful to carry out numerical computations with arbitrary potentials and diffusion tensors. One can also show that:

$$C_4 = \left\langle R^2 \right\rangle_0 - \left\langle R \right\rangle_0^2, \quad R(z) = \int_{-H}^{z} dz' \frac{J(z') \exp[\beta V(z')]}{D_\perp(z')}.$$  

(S16)

C. Analytical solutions for narrow channels

In this part, we consider the simple case where there is no potential and where the channel has a sufficiently narrow width with respect to the particle size so that the diffusion constant can be taken to vary quadratically within the channel:

$$D_\perp(z) = D_{\perp0} \left( 1 - \frac{z^2}{H^2} \right), \quad D_{\parallel}(z) = D_{\parallel0} \left( 1 - \frac{z^2}{H^2} \right).$$  

(S17)
where $H_s$ a characteristic length that can be considered as a diffusive slip length when $H_s > H$ and $D_\perp$ vanishes at $z = \pm H$. The coefficients $D_{\perp0}$ and $D_{||0}$ depend on the effective channel height $H$ and $a$. The quadratic model of the diffusion constant in the height direction has been proposed in a theoretical context by a number of authors [6, 7]. In Fig. S1(b), we have compared the superposition approximation for the local components of the diffusion tensor to simple quadratic fits for a narrow channel. As one might expect, due to the narrowness of the channel, this approximation works fairly well.

In the absence of an external potential, one has $p_0(z) = (2H)^{-1}$ and the effective longitudinal diffusion constant is given by:

$$\langle D_{||} \rangle_0 = D_{||0} \left( 1 - \frac{H^2}{3H_s^2} \right).$$  \hspace{1cm} (S18)

Using Eqs. (S15,S16), we find:

$$D_4 = \frac{2D_{||0}^2 H^6}{135D_{\perp0}H_s^4}, \quad C_4 = \frac{D_{||0}^2 H^8}{405D_{\perp0}^2 H_s^4}.$$  \hspace{1cm} (S19)

Since the diffusivities show quadratic profiles, a more detailed analysis, involving full time dependence is available. In fact, here the operator $\mathcal{H}$ (see Eq. (??)) is self adjoint and its eigenvalues and normalized eigenfunctions are given by:

$$\psi_n(z) = \sqrt{\frac{2n+1}{2H}} P_n \left( \frac{z}{H} \right), \quad \lambda_n = \frac{D_{||0}}{H^2 n(n+1)},$$  \hspace{1cm} (S20)

where $P_n$ denotes the $n^{th}$ degree Legendre polynomial.

If we write $D_{||}(z)$ in terms of Legendre polynomials, we get:

$$\frac{D_{||}(z)}{D_{||0}} = \left( 1 - \frac{H^2}{3H_s^2} \right) P_0 \left( \frac{z}{H} \right) - \frac{2H^2}{3H_s^2} P_2 \left( \frac{z}{H} \right).$$  \hspace{1cm} (S21)

From Eq. (S8), the full time dependent behavior of the fourth cumulant is then given by:

$$\frac{\langle X_4^2 \rangle_t}{24} = \frac{2D_{||0}^2 H^6}{135D_{\perp0}^2 H_s^4} t - \frac{D_{||0}^2 H^8}{405D_{\perp0}^2 H_s^4} \left[ 1 - \exp \left( -\frac{6D_{\perp0} t}{H^2} \right) \right].$$  \hspace{1cm} (S22)
which is Eq. (??) in the main text. From the latter, one can recover the late time corrections given in Eq. (S19). This solution of the fourth cumulant can be extended to arbitrary expressions of $D_\parallel$ as long as it can be expressed on the basis of Legendre polynomials:

$$D_\parallel(z) = \sum_{n=0}^{\infty} d_n P_n \left( \frac{z}{H} \right), \quad d_n = \frac{2n+1}{2} \int_{-1}^{1} d\zeta P_n(\zeta) D_\parallel(\zeta H).$$  

(S23)

The fourth cumulant reads in this general case:

$$\frac{(X_t^4)_c}{24} = \sum_{n \geq 1} \left[ \frac{H^2}{D_{\perp 0} n(n+1)} t - \frac{H^4}{D_{\perp 0}^2 n^2(n+1)^2} + \frac{H^4 e^{-\frac{D_{\perp 0} n(n+1)}{H^2} t}}{D_{\perp 0}^2 n^2(n+1)^2} \right] \frac{d_n^2}{2n+1}. \quad (S24)$$

D. Probability distribution function of lateral displacement

The probability distribution function (PDF) of the displacement $X_t$ can be analysed by considering the corresponding cumulant generating function:

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

(S25)

where in the last equality we have averaged over the Brownian increments $dB_{x,s}$ which are independent of $Z_s$. This has the form of a functional of the process $Z_s$:

$$g(\mu, t) = \langle e^{\mu \int_0^t u(Z_s) ds} \rangle,$$

(S26)

where $\mu = q^2$ and $u(z) = D_\parallel(z)$. Written this way, we see the mathematical resemblance between the diffusing diffusivity problem and Taylor dispersion in a velocity field $u(z)$:

$$Y_t = \int_0^t u(Z_s) ds,$$

(S27)

at the level of the generating functions of the two processes. The cumulant generating function, by definition, yields the cumulants of $Y_t$ via

$$g(\mu, t) = \exp \left[ \sum_{n=1}^{\infty} \frac{\mu^n}{n!} \langle Y_t^n \rangle_c \right].$$

(S28)

The functional $g(\mu, t)$ can be evaluated by using the Feynman-Kac formula [8] as $g(\mu, t) = \langle G(\mu, t, z) \rangle_0$, where $G$ satisfies the equation:

$$\frac{\partial G(\mu, t, z)}{\partial t} = [-\mathcal{H}^\dagger + \mu D_\parallel(z)] G(\mu, t, z), \quad G(\mu, t = 0, z) = 1. \quad (S29)$$

Similar equations appear for the diffusion of anisotropic objects [9, 10]. If one determines the eigenvalues $\lambda(\mu)$ of $\mathcal{H}^\dagger - \mu D_\parallel(z)$, then we obtain:

$$g(\mu, t) = \sum_{\lambda(\mu)} e^{-\lambda(\mu)t} \int_{-H}^{H} dz \ p_0(z) \phi_{R,\lambda}(z) \int_{-H}^{H} dz' \ \phi_{L,\lambda}(z'),$$

(S30)

where $\phi_{R,\lambda}, \phi_{L,\lambda}$ are respectively the right and left eigenfunctions of $\mathcal{H}^\dagger - \mu D_\parallel(z)$.

At late times, the solution is dominated by the smallest eigenvalue $\lambda_0(\mu)$ of the operator $\mathcal{H}^\dagger - \mu D_\parallel(z)$:

$$g(\mu, t) = e^{-\lambda_0(\mu)t} \int_{-H}^{H} dz \ p_0(z) \phi_{R,0}(z) \int_{-H}^{H} dz' \ \phi_{L,0}(z'),$$

(S31)

where

$$\mathcal{H}^\dagger \phi_{R,0}(z) - \mu D_\parallel(z) \phi_{R,0}(z) = \lambda_0(\mu) \phi_{R,0}(z).$$

(S32)
Note that the prefactor is obtained from the initial condition \( g(\mu, t = 0) = 1 \). Comparing with the definition (S28) of the cumulants via the generating function, this result then implies that at late times:

\[
- \lambda_0(\mu) t = \sum_{n=1}^{\infty} \frac{\mu^n}{n!} (Y^n_t)_c.
\]  

(S33)

This formula means that all cumulants of \( Y_t \) (and also all cumulants of \( X_t \)) scale as \( t \) for large times:

\[
(Y^n_t)_c \sim t^{n-1} u_n t,
\]  

(S34)

and the coefficients \( u_n \) are found by considering the series expansion of \( \lambda_0(\mu) \) near \( \mu = 0 \), hence \( u_n = - (\partial^n_{\mu} \lambda_0)_{\mu=0} \). This gives an alternative method of computing the late time behavior of the cumulants using perturbation theory and one can check that it agrees with the Kubo formula used in the Letter for the second and fourth cumulants.

E. Convergence to Gaussian statistics in the diffusive scaling regime.

The goal of this section is to establish how the PDF \( p(x, t) \) converges to a Gaussian when \( x = \xi \sqrt{t} \) (this, in the diffusive regime), in the large time limit. We notice that the Fourier transform of \( p(x, t) \) written \( \tilde{p}(k, t) \) is obtained by setting \( q = -ik \) in the moment generating function \([g(q, t) = \tilde{p}(k, t)]\). Thus, \( p \) can be recovered by taking the inverse Fourier transform of \( g \):

\[
p\left(x = \xi \sqrt{t}, t\right) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \, e^{ik\xi \sqrt{t}} \tilde{p}(k, t) = \frac{1}{2\pi \sqrt{t}} \int_{-\infty}^{\infty} dk \, e^{ik\xi} g\left(-\frac{k}{\sqrt{t}}, t\right),
\]  

(S35)

where we have set \( \tilde{k} = k \sqrt{t} \) in the second equality. Now, we may formally use Eq.(S28) to write:

\[
p\left(x = \xi \sqrt{t}, t\right) \approx \frac{1}{2\pi \sqrt{t}} \int_{-\infty}^{\infty} dk \, \exp \left[i \kappa \xi + \sum_{n=1}^{\infty} (-\tilde{k}^2)^n \frac{(Y^n_t)_c}{tn!}\right],
\]  

(S36)

\[
\approx \frac{1}{2\pi \sqrt{t}} \int_{-\infty}^{\infty} dk \, \exp \left[i \kappa \xi + \sum_{n=1}^{\infty} (-\tilde{k}^2)^n \frac{u_n t}{tn!}\right],
\]  

(S37)

where we have used the previously determined behavior \((Y^n_t)_c \sim u_n t \) at large times. We see that all terms with \( n \geq 2 \) in this expansion are proportional to \( t^{1-n} \) and can thus be treated as perturbative terms when \( t \to \infty \). In particular, keeping only the term \( n = 2 \) leads to:

\[
p\left(x = \xi \sqrt{t}, t\right) \approx \frac{1}{2\pi \sqrt{t}} \int_{-\infty}^{\infty} dk \, \exp \left[i \kappa \xi - \frac{u_2 k^4}{2t}\right].
\]  

(S38)

Using \( u_1 = \langle D\rangle_0 \) and \( u_2 = 2D_4 \) and performing the integral leads to:

\[
p\left(x = \xi \sqrt{t}, t\right) \approx \frac{1}{\sqrt{4\pi t\langle D\rangle_0}} \exp \left(-\frac{\xi^2}{4\langle D\rangle_0}\right) \left[ 1 + \frac{D_4}{16 t\langle D\rangle_0} \left[ 12\langle D\rangle_0^2 (1 - \xi^2) + \xi^4 \right] \right].
\]  

(S39)

The above derivation basically recovers the first terms of the Gram Charlier series of type A used in the analysis of non-Gaussian [11] random variables. We thus see that in the diffusive scaling regime, non-Gaussian statistics decay with time. This is of course compatible with the observation, made in the main text, that the non-Gaussianity parameter \( \alpha(t) = \langle X^4_t \rangle_c/\langle X^2_t \rangle_c^2 \sim 1/t \) at late times. In the next section, we will see that the only trace of non-Gaussian statistics at very late times is in the extreme value statistics where the central limit theorem does not apply.

F. Gaussian tail of the displacement PDF at short times

At short times, the displacement PDF reads:[12–15]

\[
p(x, t) = \int_{-H}^{H} dz \, \frac{1}{\mathcal{Z}} e^{-\beta V(z)} \times \frac{e^{-\frac{x^2}{4\pi D(z)t^2}}}{\sqrt{4\pi D(z)t}},
\]  

(S40)
where $Z = \int_{-H}^{H} dz e^{-\beta V(z)}$. In this section, we analyze the tails of $p(x,t)$ given by the above expression for the parameters of the experiment. To make analytical calculations easier, we use a simplified form for $D_\parallel(z)$ which is correct both near the wall (at leading order) and far from the wall (at next-to-leading order when $z \to \infty$)

$$D_\parallel(z) \simeq D_0 \frac{\nu + 2\tilde{z}}{2\tilde{z} + 3\nu}, \quad \nu = \frac{9a}{16},$$  \hspace{1cm} (S41)

with $\tilde{z} = z + H$, so that $\tilde{z} = 0$ corresponds to the situation where the particle touches the wall. This simplified expression differs by less than 8% from Eq. (17) in the main text. Next, we note that in our experiment the length $l_B$ is much smaller than the distance between the plates of the channel, so that we can ignore the presence of the upper-wall. Most of the contribution to $p$ for large $x$ comes from the regions where the local diffusivity is largest, hence for large $z$, where $\beta V \simeq \tilde{z}/l_B$.

We now write $p$ as

$$p(x,t) = \int_0^\infty d\tilde{z} \frac{1}{Z} e^{-f(\tilde{z})} \sqrt{4\pi D_\parallel(\tilde{z})t}, \quad f(\tilde{z}) = \frac{x^2}{4D_\parallel t} + \frac{\tilde{z}}{l_B}. \hspace{1cm} (S42)$$

Let us define $z^*$ the value of $\tilde{z}$ for which $f'(\tilde{z}) = 0$. A simple calculation shows that

$$f(z^*) = \frac{x^2}{4D_0 t} + x \sqrt{\frac{\nu}{l_B D_0 t}} - \frac{\nu}{2l_B}, \hspace{1cm} (S43)$$

and

$$f''(z^*) = 4 \frac{\sqrt{D_0 t}}{l_B^{3/2} \sqrt{\nu} x}, \quad D_\parallel(z^*) = \frac{D_0 \sqrt{l_B} x}{2\sqrt{D_0 t} + \sqrt{l_B} x}. \hspace{1cm} (S44)$$

We now evaluate $p$ in Eq. (S42) with the saddle-point method:

$$p(x,t) \simeq \frac{1}{Z} \frac{1}{\sqrt{2\pi D_\parallel(z^*)t}} e^{-f(z^*)}. \hspace{1cm} (S45)$$

We note that $f(z^*)$, given by Eq. (S43), is quadratic in $x$, so that the tail of $p$ is clearly of Gaussian form for large $x$. This expression is in excellent agreement at large $x$ with the experimental and numerical results, see Fig. 2(f) in the main text.

G. Extreme value statistics

Here, we consider contributions to the PDF at large values of $x$ corresponding to trajectories which diffuse much further than the typical (diffusive) ones. The probability of these rare events can be computed using large deviation theory. The reader is referred to [16] for a standard introduction written for physicists. If we consider the moment generating function in the form of Eq. (S25), we see that for $q$ large, paths which are highly dispersed dominate the functional. The large deviation analysis for Taylor dispersion was carried out in Refs. [17–19] and we adapt the analysis there to study the diffusing diffusivity model under consideration here.

The tails of the displacement PDF are obtained by analyzing the limit $q \to \infty$ in the moment generating function. We are sampling the large dispersion regime where $Z_t$ stays close to $z^*$ where $D_\parallel(z)$ attains its maximum. We make the physically relevant assumption that that $z^*$ is not located at the wall. We thus look for an eigenfunction $\phi_{R,0}$ that is localized near $z = z^*$. Writing $z = z^* + \frac{\zeta}{|q|^{1/2}}$, for some $\alpha > 0$, the eigenvalue equation for $\phi_{R,0}(z) = \psi_0(\zeta)$ simplifies at leading order in $q \to \infty$:

$$\left\{ |q|^{2\alpha} D_\perp(z^*) \frac{d^2}{d\zeta^2} + \lambda_0(q) + q^2 \left[ D_\parallel(z^*) - \frac{1}{2} |D_\parallel''(z^*)| \frac{\zeta^2}{|q|^{2\alpha}} \right] \right\} \psi_0(\zeta) = 0. \hspace{1cm} (S46)$$

We see that we have to take $\alpha = 1/2$ so that $\psi$ does not depend on $q$. We recognize the quantum harmonic oscillator problem, so that we directly write the lowest eigenvalue solution:

$$\psi_0(\zeta) \propto \exp \left[ -\sqrt{\frac{D_\parallel''(z^*)}{2SD_\perp(z^*)}} \zeta^2 \right], \quad \lambda_0(q) = |q| \sqrt{\frac{|D_\parallel''(z^*)|D_\perp(z^*)}{2}} - q^2 D_\parallel(z^*). \hspace{1cm} (S47)$$
If we assume the large deviation form of \( p(x, t) \sim e^{-tf(x/t)} \) (up to exponential prefactors), we find that

\[
g(q, t) \sim \int dx \ e^{-t(f(x)+q x)} \sim \int d\xi \ e^{t[q\xi-f(\xi)\xi]} \sim \exp\left\{ \max_{\xi} [q\xi-f(\xi)\xi] \right\},
\]

where we have used the saddle point method and the notation \( \xi = x/t \). Since we already know that \( g(q, t) \propto \exp[-t\lambda_0(q)] \), we see that

\[
-\lambda_0(q) = \max_{\xi} [q\xi-f(\xi)].
\]

Hence, the minimal eigenvalue \(-\lambda_0(q)\) is the Legendre transform of the large deviation function \( f \) [17–19]. Inverting the Legendre transform we obtain:

\[
f(\xi) = \max_q [q\xi + \lambda_0(q)].
\]

The behavior of \( f \) for large \( x \) is obtained by taking the Legendre transform of \( \lambda_0(q) \) for large \( |q| \) given by Eq. (S47), this leads to:

\[
f(\xi) \underset{|\xi|\to\infty}{=} \frac{1}{4D_{||}(z^*)} \left[ \xi + \text{sign}(\xi) \sqrt{D_{\perp}(z^*)/2} \right]^2 + O(1),
\]

which is Eq. (??) in the main text. This means that the PDF of the displacement \( p(x, t) \sim e^{-tf(x/t)} \) has the form of a shifted Gaussian, with a diffusivity given by the maximal value \( D_{||}(z^*) \), however the weight of these paths is strongly suppressed by the way the Gaussian is centered.

Finally, the large deviation function for small \( \xi \) can be simply computed from the second moment and reads:

\[
f(\xi) = \frac{\xi^2}{4(D_{||})_0},
\]

which matches with the result in the diffusive regime where \( x = O(\sqrt{t}) \).

### II. EXPERIMENTAL DETAILS

The experimental data presented in the main text corresponds to spherical polystyrene colloids of nominal radius 1.5 \( \mu \text{m} \) purchased from Polybead\textsuperscript{©}. The ensemble of particles that are tracked have reached their equilibrium distribution due to the lag time between the insertion of the particles and the beginning of the measurement protocol. In the latter, a single sphere is three-dimensionally tracked using a self-calibrated interferometric method based on Mie Holography [15].

A previously-calibrated plane wave (wavelength 532 nm) illuminates a dilute colloidal suspension. The light scattered by a given particle interferes with the incident beam in the focal plane of a \( \times 100 \)-objective and the interference pattern, called hologram, is magnified toward a CCD camera. Then, the strong dependencies of a hologram on both the physical properties and the position of the sphere lead to the precise measurement of the aforementioned characteristics. The first 10000 holograms are fitted to determine the physical properties of the sphere, namely its radius and optical index. Those physical properties are then set and all the holograms are fitted, leading to the trajectory of the sphere, and, after its statistical analysis, to the observables depicted in the main text.

The experimental equilibrium PDF \( p_0 \) shown in ??(a) of the main text is obtained by binning the \( z \) position of the sphere on a logarithmic normal grid.

The ensemble averages required in the computation of the experimental second and fourth cumulants (see ?????) depicted in ??(c,d) of the main text, are obtained through sliding temporal averages, assuming ergodicity:

\[
\langle X^n_t \rangle = \frac{1}{N} \sum_{j=0}^{N-1} [x(t+j) - x(t_j)]^n \equiv \frac{1}{N} \sum_{j=0}^{N-1} [\Delta x(t \mid t_j)]^n,
\]

where \( n, N \in \mathbb{N}, x(t) \) is the \( x \) position of the sphere at time \( t \), and where \( t_j = j f_a^{-1} \) with the frame rate \( f_a = 100 \) Hz of the acquisition.
The experimental local diffusion coefficients depicted in ??(b) of the main text are obtained by a stochastic force inference algorithm [20]. An unbiased estimator \( \hat{d} \) of the local diffusion coefficient in the \( x \) direction (the adaptation to the \( z \) direction being straightforward) is built as follows:

\[
\hat{d}(t_j) = \frac{[\Delta x(\delta t \mid t_{j-1}) + \Delta x(\delta t \mid t_j)]^2}{4\delta t} + \frac{\Delta x(\delta t \mid t_{j-1}) \Delta x(\delta t \mid t_j)}{2\delta t},
\]

(S54)

where \( \delta t \) is a chosen multiple of \( f_a^{-1} \) and \( \Delta x(\delta t \mid t_j) \) is the distance travelled by the sphere over a time \( \delta t \) and starting at \( t_j \). Each of the above values of \( \hat{d} \) corresponds to a given height \( H + z \) and their distribution is estimated on a normal grid \( \{\hat{z}\} \) with a polynomial function basis of order 3: \( \sum a_k(\hat{z})(H + z)^k \), in which the \( a_k \) are real functions. The accuracy of the method is confirmed \textit{a posteriori} by the agreement with the theoretical predictions, as shown in ???. We also note that the first term on the right-hand side of Eq. (S54) arises from the temporal linearity of the MSD (see ?? of the main text) while the second one is a correction that allows us to estimate accurately the local diffusion coefficients close to the surface \((H + z \leq 100\, \text{nm})\) where the experimental data is scarce.

Finally, several observables that stem from the sphere’s trajectory — which include the ones described above — depend on the physical parameters of the system, namely \( B \), \( l_p \) and \( l_T \) defined in ?? of the main text. These parameters are thus fitted simultaneously to increase the method’s precision.

III. NUMERICAL SIMULATIONS

We consider hereafter the three overdamped Langevin equations:

\[
\begin{align*}
\frac{dX_t}{dt} &= \sqrt{2D_{\parallel}(Z_t)} \, dB_{x,t} \\
\frac{dY_t}{dt} &= \sqrt{2D_{\parallel}(Z_t)} \, dB_{y,t} \\
\frac{dZ_t}{dt} &= D_{\perp}^{'}(Z_t)dt - \beta D_{\perp}(Z_t)V'(Z_t)dt + \sqrt{2D_{\perp}(Z_t)} \, dB_{z,t},
\end{align*}
\]

(S55)

where the first right-hand-side term of the last equation corresponds to the spurious force in the Ito convention, and where \( dB_{x,t} \), \( dB_{y,t} \) and \( dB_{z,t} \) are independent Brownian increments. The simulation takes into account the bottom and top walls positioned at \( \pm H_p \). The potential \( V(z) \) is given by Eq. (??) of the main text.

The effective viscosity perpendicular to a single wall is given by Eq. (??) of the main text. In the case of the relatively wide channel studied experimentally, we can use the superposition approximation and estimate the excess drag forces with respect to the bulk ones as the sum of the corresponding contributions from the individual surfaces. The total effective viscosities are thus given by:

\[
\mu^T_i(z) - \mu_0 \simeq \mu^+_{i}(z) - \mu_0 + \mu^-_{i}(z) - \mu_0,
\]

(S56)

with \( i \in \{\|, \perp\} \), and where \( \mu^\pm_i(z) \) denote the individual effective viscosities near both walls. The Stokes-Einstein relation then gives:

\[
D_i(z) \simeq \frac{k_B T}{6\pi a [\mu^+_i(z) + \mu^-_i(z) - \mu_0]}.
\]

(S57)

We plot \( D_{\|}(z) \) and \( D_{\perp}(z) \) for \( H_p = 40\, \mu\text{m} \) in Fig. S1(a), and for \( H_p = 5.5\, \mu\text{m} \) in Fig. S1(b). Also shown for comparison are the parabolic approximations for the narrow-channel case.

We discretize Eq. (S55) by using an Euler scheme where solutions are approximated by \( X_i(t) \approx X_n(t_n), \ Y_i(t) \approx Y_n(t_n), \ Z_i(t) \approx Z_n(t_n) \), with \( t_n = n\Delta t, \ \Delta t \) being the simulation time step. The increments \( dB_{k,t} \) \((k \in \{x, y, z\})\) are approximated by \( \Delta B_{k,n} = W_{k,n} \), where \( W_{k,n} \) are independent Gaussian-distributed random variables of zero mean and unit variance. This leads to the discrete stochastic equations:

\[
\begin{align*}
X_{n+1} &= X_n + \sqrt{2D_{\parallel}(Z_n)} \, W_{x,n} \sqrt{\Delta t} \\
Y_{n+1} &= Y_n + \sqrt{2D_{\parallel}(Z_n)} \, W_{y,n} \sqrt{\Delta t} \\
Z_{n+1} &= Z_n + D_{\perp}^{'}(Z_n)\Delta t - \beta D_{\perp}(Z_n)V'(Z_n)\Delta t + \sqrt{2D_{\perp}(Z_n)} \, W_{z,n} \sqrt{\Delta t}.
\end{align*}
\]

(S58)
FIG. S2. Fourth cumulant (a), and rescaled fourth cumulant (b) as functions of time, for $H_p = 40 \mu m$. Green stars: experimental data. Blue dots: simulation data. Orange solid and dashed lines: asymptotic predictions (see main text). Solid black lines: exact theory at all times (see main text). The three last panels correspond to the PDF $p(x,t)$ for (c) $t = \tau_1 = 0.01s$, (d) $t = \tau_2 = 1.09s$ and (e) $t = \tau_3 = 95.4 s$. Green stars: experimental data. Blue dots: simulation data. Grey dashed lines: late time Gaussian distribution given by the first term of Eq. (S39). Solid black lines: exact prediction obtained by numerically inverting the Fourier transform $\hat{p}(k,t) = g(q = -ik,t)$ given by Eq. (S31).

We numerically integrate (S58) with $\Delta t = 0.01 s$, for a total time of 1000 s, with identical physical parameters as the experimental ones. The system is allowed to first equilibrate in the vertical direction. From approximately 12 million trajectories, we extract the numerical fourth cumulant $\langle X^4_t \rangle_c$ at all times using the PDF $p(x,\tau)$ of displacements $x = X_{t+\tau} - X_t$ generated from sliding temporal averaging. Specifically, the fourth cumulant is numerically calculated from:

$$\langle X^4_{t+\Delta \tau} \rangle_c = \int_{-\infty}^{+\infty} u^4 P(u, \Delta \tau) du - 3 \left[ \int_{-\infty}^{+\infty} u^2 P(u, \Delta \tau) du \right]^2.$$  \hspace{1cm} (S59)

Finally, as shown in ??(d) of the main text and in Fig. S2, the numerical results are in good agreement with both theoretical and experimental results, for a channel with $H_p = 40 \mu m$. We have also carried out numerical simulations for a much narrower channel, i.e. with $H_p = 5.5 \mu m$, but otherwise using the same parameters as the ones in the
FIG. S3. Fourth cumulant (a), and rescaled fourth cumulant (b) as functions of time, for $H_p = 5.5 \mu m$. Blue dots: simulation data. Orange solid and dashed lines: asymptotic predictions (see main text). Solid black lines: exact theory at all times (see main text). The three last panels correspond to the PDF $p(x,t)$ for (c) $t = \tau_1 = 0.01s$, (d) $t = \tau_2 = 1.09s$ and (e) $t = \tau_3 = 95.4s$. Blue circles: simulation data. Grey dashed lines: late time Gaussian distribution given by the first term of Eq. (S39). Solid black lines: exact prediction obtained by numerically evaluating the expression of $p$ at short-times given by Eq. (S40).

experimental setup. The results are shown in Fig. S3.

[1] Alexandre, A., Guérin, T. & Dean, D. S. Generalized Taylor dispersion for translationally invariant microfluidic systems. Phys. Fluids 33, 082004 (2021).
[2] Gardiner, C. W. Stochastic methods for physics, and handbook for the natural and social sciences (Springer Series in Synergetics, 2009).
[3] Guérin, T. & Dean, D. S. Force-induced dispersion in heterogeneous media. Phys. Rev. Lett. 115, 020601 (2015).
[4] Guérin, T. & Dean, D. S. Kubo formulas for dispersion in heterogeneous periodic nonequilibrium systems. Phys. Rev. E 92, 062103 (2015).
[5] Brenner, H. & Edwards, D. A. Macrotransport Processes (Butterworth-Heinemann, 1993).
[6] Lau, A. W. & Lubensky, T. C. State-dependent diffusion: Thermodynamic consistency and its path integral formulation. Phys. Rev. E 76, 011123 (2007).
[7] Avni, Y., Komura, S. & Andelman, D. Brownian motion of a charged colloid in restricted confinement. Phys. Rev. E 103, 042607 (2021).
[8] Øksendal, B. Stochastic differential equations (Springer, New-York, 2003).
[9] Munk, T., Höfling, F., Frey, E. & Franosch, T. Effective perrin theory for the anisotropic diffusion of a strongly hindered...
rod. EPL (Europhysics Letters) 85, 30003 (2009).

[10] Kurzthaler, C., Leitmann, S. & Franosch, T. Intermediate scattering function of an anisotropic active brownian particle. Scientific reports 6, 1–11 (2016).

[11] Cramér, H. Mathematical methods of statistics (Princeton university press, 1946).

[12] Chubynsky, M. V. & Slater, G. W. Diffusing diffusivity: A model for anomalous, yet brownian, diffusion. Phys. Rev. Lett. 113, 098302 (2014).

[13] Han, Y. et al. Brownian motion of an ellipsoid. Science 314, 626–630 (2006).

[14] Chechkin, A. V., Seno, F., Metzler, R. & Sokolov, I. M. Brownian yet non-gaussian diffusion: from superstatistics to subordination of diffusing diffusivities. Phys. Rev. X 7, 021002 (2017).

[15] Lavaud, M., Salez, T., Louyer, Y. & Amarouchene, Y. Stochastic inference of surface-induced effects using brownian motion. Phys. Rev. Res. L032011 (2021). Publisher: APS.

[16] Touchette, H. The large deviation approach to statistical mechanics. Phys. Rep. 478, 1–69 (2009).

[17] Haynes, P. & Vanneste, J. Dispersion in the large-deviation regime. part 2. cellular flow at large péclet number. J. Fluid Mech. 745, 351–377 (2014).

[18] Haynes, P. & Vanneste, J. Dispersion in the large-deviation regime. part 1: shear flows and periodic flows. J. Fluid Mech. 745, 321–350 (2014).

[19] Kahlen, M., Engel, A. & Van den Broeck, C. Large deviations in taylor dispersion. Phys. Rev. E 95, 012144 (2017).

[20] Frishman, A. & Ronceray, P. Learning force fields from stochastic trajectories. Phys. Rev. X 10, 021009 (2020).