Supplementary Material for Non-Gaussian diffusion near surfaces

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THEORETICAL FORMALISM

Cumulants of the horizontal displacement

The fourth cumulant is obtained by direct computation

$$\langle X_t^4\rangle_{\rm c} \equiv \langle X_t^4\rangle - 3\langle X_t^2\rangle^2 = 12\int_0^t {\rm d}s \int_0^t {\rm d}s'\ \langle D_\parallel(Z_s)D_\parallel(Z_{s'})\rangle - \langle D_\parallel(Z_s)\rangle\langle D_\parallel(Z_{s'})\rangle, \tag{S1}$$

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

$$\begin{aligned}\langle X_t^4\rangle_{\rm c} &= 12\int_0^t {\rm d}s \int_0^t {\rm d}s' \left\langle \left[D_\parallel(Z_s) - \left\langle D_\parallel(Z_s)\right\rangle\right]\left[D_\parallel(Z_{s'}) - \left\langle D_\parallel(Z_{s'})\right\rangle\right]\right\rangle \\ &= 12\left\langle \left[\int_0^t {\rm d}s\ D_\parallel(Z_s) - \left\langle D_\parallel(Z_s)\right\rangle\right]^2\right\rangle.\end{aligned} \tag{S2}$$

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 $\langle X_t^4\rangle_{\rm c}$ is 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. (1) of the main text, with the initial condition $p(z|z';0) = \delta(z-z')$. In this framework, for the process X_t starting from equilibrium, one has:

$$\langle X_t^4\rangle_{\rm c} = 24\int_0^t {\rm d}s \int_0^s {\rm d}s' \int_{-H}^H {\rm d}z\, D_\parallel(z)\int_{-H}^H {\rm d}z' D_\parallel(z')\left[p(z|z';s-s') - p_0(z)\right]p_0(z'). \tag{S4}$$

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

$$\begin{cases} \mathcal{H}^\dagger\psi_{{\rm L}\lambda} &= \lambda\psi_{{\rm L}\lambda}, \\ \mathcal{H}\psi_{{\rm R}\lambda} &= \lambda\psi_{{\rm R}\lambda}, \end{cases} \tag{S5}$$

with λ 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

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

The right eigenfunctions satisfy the no-flux boundary condition

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

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

$$\langle X_t^4\rangle_{\rm c} = 24\int_{-H}^H {\rm d}z \int_{-H}^H {\rm d}z'\, D_\parallel(z)D_\parallel(z')p_0(z')\sum_{\lambda>0}\left[\frac{t}{\lambda} - \frac{1}{\lambda^2} + \frac{\exp(-\lambda t)}{\lambda^2}\right]\psi_{{\rm R}\lambda}(z)\psi_{{\rm L}\lambda}(z'), \tag{S8}$$

which is Eq. (5) 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 $\langle X_t^4\rangle_{\rm c}$. In contrast, the short-time and long-time behaviors can be extracted analytically from Eq. (S8), as explained in the following subsection.

Asymptotic behavior of the fourth cumulant

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

$$\langle X_t^4 \rangle_{\rm c} \underset{t\to 0}{\simeq} 12\, t^2 \int_{-H}^{H} {\rm d}z \int_{-H}^{H} {\rm d}z' D_\parallel(z) D_\parallel(z') p_0(z') \sum_{\lambda>0} \psi_{{\rm R}\lambda}(z) \psi_{{\rm L}\lambda}(z'). \tag{S9}$$

Furthermore, the completeness relation leads to:

$$\sum_{\lambda>0} \psi_{{\rm R}\lambda}(z) \psi_{{\rm L}\lambda}(z') = \delta(z-z') - p_0(z). \tag{S10}$$

Then, Eq. (S9) becomes

$$\left\langle X_t^4 \right\rangle_{\rm c} \underset{t\to 0}{\simeq} 12\, t^2 \left[\left\langle D_\parallel^2 \right\rangle_0 - \left\langle D_\parallel \right\rangle_0^2 \right]. \tag{S11}$$

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 λ_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:

$$\langle X_t^4 \rangle_{\rm c} \underset{t\to +\infty}{\simeq} 24 \left(D_4 t - C_4 \right), \tag{S12}$$

with

$$D_4 = \int_{-H}^{H} {\rm d}z \int_{-H}^{H} {\rm d}z' D_\parallel(z) D_\parallel(z') p_0(z') \sum_{\lambda>0} \frac{\psi_{{\rm R}\lambda}(z) \psi_{{\rm L}\lambda}(z')}{\lambda}, \tag{S13}$$

and

$$C_4 = \int_{-H}^{H} {\rm d}z \int_{-H}^{H} {\rm d}z' D_\parallel(z) D_\parallel(z') p_0(z') \sum_{\lambda>0} \frac{\psi_{{\rm R}\lambda}(z) \psi_{{\rm L}\lambda}(z')}{\lambda^2}. \tag{S14}$$

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

$$D_4 = \left\langle \frac{\left(J e^{\beta V} \right)^2}{D_\perp} \right\rangle_0, \tag{S15}$$

with

$$J(z) = \int_{-H}^{z} {\rm d}z' \exp[-\beta V(z')] [D_\parallel(z') - \langle D_\parallel \rangle_0]. \tag{S16}$$

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

$$C_4 = \left\langle R^2 \right\rangle_0 - \langle R \rangle_0^2, \tag{S17}$$

with

$$R(z) = \int_{-H}^{z} {\rm d}z' \; \frac{J(z') \exp\left[\beta V(z')\right]}{D_\perp(z')}. \tag{S18}$$

Analytical solutions

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:

$$D_\perp(z) = D_{\perp 0}\left(1 - \frac{z^2}{H^2}\right),\ D_{||}(z) = D_{||0}\left(1 - \frac{z^2}{H_\mathrm{s}^2}\right), \tag{S19}$$

where H_s a characteristic length that can be considered as a diffusive slip length when $H_\mathrm{s} > H$ and $D_\perp$ vanishes at $z = \pm H$. The coefficients $D_{\perp 0}$ 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 the absence of an external potential, one has $p_0(z) = (2H)^{-1}$ and the effective longitudinal diffusion constant is given by

$$\left\langle D_{||}\right\rangle_0 = D_{||0}\left(1 - \frac{H^2}{3H_\mathrm{s}^2}\right). \tag{S20}$$

Using the results from section (S15, S17), we find that

$$D_4 = \frac{2D_{||0}^2 H^6}{135 D_{\perp 0} H_\mathrm{s}^4},\ C_4 = \frac{D_{||0}^2 H^8}{405 D_{\perp 0}^2 H_\mathrm{s}^4}. \tag{S21}$$

Since the diffusivities show quadratic profiles, a more detailed analysis, involving full time dependence is available. In fact, the operator $\mathcal{H}$ (see Eq. (1)) is self adjoint and its normalized eigenfunctions are given by

$$\psi_n(z) = \sqrt{\frac{2n+1}{2H}}\ P_n\left(\frac{z}{H}\right), \tag{S22}$$

where P_n denotes the n^{th} degree Legendre polynomial, with associated eigenvalue:

$$\lambda_n = \frac{D_{||0}}{H^2} n(n+1). \tag{S23}$$

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

$$\frac{D_{||}(z)}{D_{||0}} = \left(1 - \frac{H^2}{3H_\mathrm{s}^2}\right) P_0\left(\frac{z}{H}\right) - \frac{2H^2}{3H_\mathrm{s}^2} P_2\left(\frac{z}{H}\right). \tag{S24}$$

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

$$\frac{\langle X_t^4\rangle_\mathrm{c}}{24} = \frac{2D_{||0}^2 H^6}{135 D_{\perp 0} H_\mathrm{s}^4} t - \frac{D_{||0}^2 H^8}{405 D_{\perp 0}^2 H_\mathrm{s}^4}\left[1 - \exp\left(-\frac{6D_{\perp 0} t}{H^2}\right)\right]. \tag{S25}$$

which is Eq. (18) in the main text. From the latter, one can recover the late time corrections given in Eq. (S21).

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:

$$D_{||}(z) = \sum_{n=0}^{\infty} d_n P_n\left(\frac{z}{H}\right), \tag{S26}$$

with

$$d_n = \frac{2n+1}{2}\int_{-1}^{1} \mathrm{d}\zeta\ P_n(\zeta) D_{||}(\zeta H). \tag{S27}$$

The fourth cumulant reads in this general case:

$$\frac{\langle X_t^4\rangle_\mathrm{c}}{24} = \sum_{n\geq 1}\left[\frac{H^2}{D_{\perp 0} n(n+1)} t - \frac{H^4}{D_{\perp 0}^2 n^2 (n+1)^2} + \frac{H^4 \exp(-\frac{D_{\perp 0}}{H^2} n(n+1) t)}{D_{\perp 0}^2 n^2 (n+1)^2}\right]\frac{d_n^2}{2n+1}. \tag{S28}$$

EXPERIMENTAL DETAILS

The experimental data presented in the main text corresponds to spherical polystyrene spheres of nominal radius 1.5 μm purchased from Polybead©. A single sphere is 3-dimensionally tracked using a self-calibrated interferometric method based on Mie Holography [8].

A previously-calibrated plane wave (wavelength 532 nm) illuminates a dilute sphere suspension. The light scattered by the interesting sphere interferes with the incident beam in the focal plane of a x100-objective and the interference pattern, called hologram, is magnified toward a CCD camera. Then, the strong dependency of a hologram on both the physical properties and the position of the sphere leads 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 Fig. 2(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, defined in the first equalities of Eqs. (6) and (7) and depicted in Fig. 2(c,d) of the main text, are obtained through sliding temporal averages, assuming ergodicity:

$$\langle X_t^n \rangle = \frac{1}{N} \sum_{j=0}^{N-1} \left[x(t+t_j) - x(t_j) \right]^n \equiv \frac{1}{N} \sum_{j=0}^{N-1} \left[\Delta x(t \,|\, t_j) \right]^n , \tag{S29}$$

where $n, N \in \mathbb{N}$, $x(t)$ is the x position of the sphere at time t and $t_j = j\, f_{\mathrm{a}}^{-1}$ with $f_{\mathrm{a}} = 100$ Hz the frame rate of the acquisition.

The experimental local diffusion coefficients depicted in Fig. 2(b) of the main text are obtained by a stochastic force inference algorithm [9]. 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:

$$\hat{d}(t_j) = \frac{\left[\Delta x(\delta t \,|\, t_{j-1}) + \Delta x(\delta t \,|\, t_j) \right]^2}{4\delta t} + \frac{\Delta x(\delta t \,|\, t_{j-1}) \Delta x(\delta t \,|\, t_j)}{2\delta t}, \tag{S30}$$

where δt is a chosen multiple of f_a^{-1} and $\Delta x(\delta t \,|\, t_j)$ is the distance traveled by the sphere over a time δt 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 $\{\tilde{z}\}$ with a polynomial function basis of order 3 $\sum a_k(\tilde{z})(H+z)^k$, in which the a_k are real functions. The accuracy of the method is confirmed *a posteriori* by the agreement with the theoretical predictions, as shown in Fig. 2. Besides, note that the first term on the right-hand side of Eq. (S30) arises from the temporal linearity the MSD (see Eq. (6) of the main text) while the second one is a correction that allows to estimate accurately the local diffusion coefficients close to the surface ($H + z \leq 100$ nm) where the experimental data is not abundant.

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_{D} and l_{B} defined in Eq. (19) of the main text, and are thus fitted simultaneously to increase the method's precision.

NUMERICAL SIMULATIONS

We consider hereafter the three overdamped Langevin equations:

$$\begin{cases} \mathrm{d}X_t = \sqrt{2D_{\parallel}(Z_t)}\, dB_{x,t}, \\ \mathrm{d}Y_t = \sqrt{2D_{\parallel}(Z_t)}\, dB_{y,t}, \\ \mathrm{d}Z_t = D'_{\perp}(Z_t)dt - \beta D_{\perp}(Z_t)V'(Z_t)dt + \sqrt{2D_{\perp}(Z_t)}\, dB_{z,t}, \end{cases} \tag{S31}$$

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 $\pm H_{\mathrm{p}}$. The potential $V(z)$ is given by Eq. (19) of the letter.

The friction coefficient perpendicular to a single wall given by Eq. (20) of the letter and in the case of the relatively wide channel studied experimentally we can use the superposition approximation which approximates the excess drag force, with respect to the bulk, due to two widely separated surfaces as the sum of the excess drag from the individual surfaces. That is to say that the total drag when there are two surfaces is given by $\mu_i^T(z)$

$$\mu_i^T(z) - \mu_0 \simeq \mu_i^+(z) - \mu_0 + \mu_i^-(z) - \mu_0, \tag{S32}$$

with $i \in \{\parallel, \perp\}$ and $\mu_i^{\pm}(z)$ denotes the drag generated by the upper and lower walls. The Stokes-Einstein relation then gives

$$D_i(z) \simeq \frac{k_{\mathrm{B}}T}{6\pi a\left[\mu_i^+(z) + \mu_i^-(z) - \mu_0\right]}. \tag{S33}$$

We discretize Eq. (S31) by using an Euler scheme where solutions are approximated by $X_t(t) \approx X_n(t_n)$, $Y_t(t) \approx Y_n(t_n)$ and $Z_t(t) \approx Z_n(t_n)$, with $t_n = n\Delta t$, Δt being the simulation time step. The Brownian increments white noise $dB_{k,t}$ ($k \in \{x, y, z\}$) are approximated $\Delta B_{k,n} = W_{k,n}$ where W_{k_n} are independent Gaussian distributed random variables of zero mean and unit variance. This leads to the discrete stochastic equation:

$$\begin{cases} X_{n+1} = X_n + \sqrt{2D_\parallel(Z_n)}\, W_{x,n}\sqrt{\Delta t}, \\ Y_{n+1} = Y_n + \sqrt{2D_\parallel(Z_n)}\, W_{y,n}\sqrt{\Delta t}, \\ Z_{n+1} = Z_n + D'_\perp(Z_n)\Delta t - \beta D_\perp(Z_n)V'(Z_n)\Delta t + \sqrt{2D_\perp(Z_n)}\, W_{z,n}\sqrt{\Delta t}. \end{cases} \tag{S34}$$

We numerically solve (S34) with $\Delta t = 0.01$ s, for a total time of 1000 s, with identical physical parameters as the experimental ones. From approximately 12 millions trajectories, we extract the numerical fourth cumulant $\langle X_t^4\rangle_{\mathrm{c}}$ at all times using the PDF of displacements $X_{t+\Delta\tau} - X_t$ written $p(u, \Delta\tau)$ generated from the histogram of sliding temporal averaging. The fourth cumulant is calculated numerically using the formula

$$\langle X_{t=\Delta\tau}^4\rangle_{\mathrm{c}} = \int_{-\infty}^{+\infty} u^4 P(u, \Delta\tau)\,\mathrm{d}u - 3\left[\int_{-\infty}^{+\infty} u^2 P(u, \Delta\tau)\mathrm{d}u\right]^2. \tag{S35}$$

Finally, as shown in Fig. 2-d), the numerical results are in good agreement with both the theoretical and experimental results.

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