Stochastic Inference of Surface-Induced Effects using Brownian Motion

Maxime Lavaud, Thomas Salez, Yann Louyer, Yacine Amarouchene

To cite this version:

Maxime Lavaud, Thomas Salez, Yann Louyer, Yacine Amarouchene. Stochastic Inference of Surface-Induced Effects using Brownian Motion. Physical Review Research, 2021, 3, pp.L032011. hal-03047058v2

HAL Id: hal-03047058
https://hal.science/hal-03047058v2
Submitted on 28 Apr 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Brownian motion is a central paradigm in modern science. It has implications in fundamental physics, biology, and even finance, to name a few. By understanding that the apparent erratic motion of colloids is a direct consequence of the thermal motion of surrounding fluid molecules, pioneers like Einstein and Perrin provided decisive evidence for the existence of atoms [1, 2]. Specifically, free Brownian motion in the bulk is characterized by a typical spatial extent evolving as the square root of time, as well as Gaussian displacements.

At a time of miniaturization and interfacial science, and moving beyond the idealized bulk picture, it is relevant to consider the added roles of boundaries to the above context. Indeed, Brownian motion at interfaces and in confinement is a widespread practical situation in microbiology and nanofluidics. In such a case, surface effects become dominant and alter drastically the Brownian statistics, with key implications towards: i) the understanding and smart control of the interfacial dynamics of microscale entities; and ii) high-resolution measurements of surface forces at equilibrium. Interestingly, a confined colloid will exhibit non-Gaussian statistics in displacements, due to the presence of multiplicative noises induced by the hindered mobility near the wall [3–5]. Besides, the particle can be subjected to electrostatic or Van der Waals forces [6] exerted by the interface, and might experience slippage too [7, 8]. Considering the two-body problem, the nearby boundary can also induce some effective interaction [9]. Previous studies have designed novel methods to measure the diffusion coefficient of confined colloids [10–15], or to infer surface forces [16–21]. However, such a statistical inference is still an experimental challenge, and a precise calibration-free method taking simultaneously into account the whole ensemble of relevant properties, over broad spatial and time ranges, is currently lacking.

In this Letter, we aim at filling the previously-identified gap by implementing a novel method of statistical inference on a set of trajectories of individual microparticles recorded by holographic microscopy. The buoyant particles are free to evolve within salty aqueous solutions, near a rigid substrate, and in the presence of surface charges. We primarily reconstruct the equilibrium probability distribution function of the position, as well as the time-resolved probability distribution functions of the displacements in directions transverse and normal to the wall, including in particular the mean-squared displacements. Special attention is dedicated to the non-Gaussian statistics, for time scales broadly ranging from tens of milliseconds to several tens of minutes. Furthermore, we implement the advanced inference method recently proposed [22]. Besides, an optimization scheme is used in order to determine precisely all the...
free physical parameters and the actual distance to the wall, at once. All together, this procedure leads to the robust calibration-free inference of the two central quantities of the problem: i) the space-dependent short-term diffusion coefficients, with a nanoscale spatial resolution; and ii) the total force experienced by the particle, at the thermal-noise limited femtoNewton resolution. These main results are summarized in Fig. 1, the goal of the Letter being the detailed obtention of which.

The experimental setup is schematized in Fig. 2a). A sample consists of a parallelepipedic chamber ($1.5 \text{ cm} \times 1.5 \text{ cm} \times 150 \mu\text{m}$), made from two glass covers, a parafilm spacer, and sealed with vacuum grease, containing a dilute suspension of spherical polystyrene beads (Sigma Aldrich) with nominal radii $a = 1.5 \pm 0.035 \mu\text{m}$, at room temperature $T$, in distilled water (type 1, MilliQ device) of viscosity $\eta = 1 \text{ mPa.s}$. The sample is illuminated by a collimated laser beam with a $532 \mu\text{m}$ wavelength. The light scattered by one colloidal particle at a given time $t$ interferes with the incident beam. An oil-immersion objective lens ($x60$ magnification, $1.30$ numerical aperture) collects the resulting instantaneous interference pattern, and relays it to a camera. The exposure time for each frame is fixed to $3 \text{ ms}$ to avoid motion-induced blurring of the image. The angular average of the intensity profile from each time frame is then fitted (see Figs. 2c,d)) to the Lorenz-Mie interference pattern [23–26], providing the particle's position $\mathbf{r} = (x, y, z)$. To reduce the uncertainty on the position measurement, we first calibrate $a = 1.518 \pm 0.006 \mu\text{m}$ and $n = 1.584 \pm 0.006$ separately from the first $10^5$ time frames. The obtained refractive index is consistent with the one reported in [15]. Then, for each subsequent time frame, the only remaining fitted quantity is $\mathbf{r}$, which allows us to reconstruct the trajectory $\mathbf{r}(t)$ with a nanometric spatial resolution, as shown in Fig. 3a).

Using the trajectory of the particle, one can then construct the equilibrium probability density function $P_{eq}(\mathbf{r})$ of the position of the particle. We find that it does not depend on $x$ and $y$, but only on the distance $z$ between the particle and the wall. As seen in Fig. 3b), an exponential tail is observed at large distance, which is identified to the sedimentation contribution in Perrin's experiment [2], but here with the probability density function of a single particle instead of the concentration field. In contrast, near the wall, we observe an abrupt depletion, indicating a repulsive electrostatic contribution. Indeed, when immersed in water, both the glass substrate and the polystyrene bead are negatively charged. All together, the total potential energy $U(z)$ thus reads:

$$
\frac{U(z)}{k_B T} = \begin{cases} 
B e^{-\frac{z}{\ell_B}} + \frac{z}{\ell_B}, & \text{for } z > 0 \\
+\infty, & \text{for } z \leq 0 
\end{cases},
$$

(1)

where $k_B$ is the Boltzmann constant, $B$ is a dimensionless number related to the surface electrostatic potentials of the particle and the wall [16], $\ell_B$ is the Debye length, $\ell_B = k_B T/(g\Delta m)$ is the Boltzmann length, $g$ is the gravitational acceleration, and $\Delta m$ is the (positive) buoyant mass of the particle. From this total potential energy, one can then construct the Gibbs-Boltzmann distribution $P_{eq}(z) = A \exp[-U(z)/(k_B T)]$ in position, where $A$ is a normalization constant, that fits the data very well, as shown in Fig. 3b). Moreover, as shown in the inset of Fig. 3b), we verified that we recover the Debye relation $\ell_D = 0.304/\sqrt{[\text{NaCl}]}$, with $\ell_D$ in nm, and where [NaCl] is the concentration of salt in mol/L, with a prefactor corresponding to a single monovalent salt in water at room temperature [27]. Besides, we have verified (not shown) that the dimensionless parameter $B = 4.8$ related to surface charges is constant in the studied salt-concentration range, thus excluding any nonlinear effect [20] in our case.

We now turn to dynamical aspects, by considering the mean-squared displacement (MSD). For the three spatial directions, indexed by $i = x, y,$ and $z$, corresponding to the coordinates $r_x = x, r_y = y,$ and $r_z = z$, of the position $\mathbf{r}$, and for a given time increment $\Delta t$, the MSD is defined as:

$$
\langle \Delta r_i(t)^2 \rangle_{\Delta t} = \langle [r_i(t + \Delta t) - r_i(t)]^2 \rangle_{\Delta t},
$$

(2)

where the average $\langle \rangle_{\Delta t}$ is performed over time $t$. For a free Brownian motion in the bulk, and in the absence of
By fitting to Eq. (5), using Eqs. (1) and (3), we extract the MSD measured along the Boltzmann distribution in position. As shown in Fig. 4a, the average diffusion coefficient \( D \) is constant over time, which is consistent with the expected linear behavior in time.

The inset shows the measured Debye length \( \xi = a^2/\eta \), where \( a = 16 \text{ nm} \) is the radius of the particle and \( \eta \) is the viscosity. The Debye length is expected to be a function of the salt concentration [NaCl]. The solid line is the expected Debye relation \( \xi = 0.304/\sqrt{[\text{NaCl}]} \), for a single monovalent salt in water at room temperature.

The presence of a rigid wall at \( z = 0 \) adds a repulsive electrostatic force along \( z \). The temporal linearity of the MSD is not altered by the presence of the wall, except for the vertical diffusion \( z \). The vertical diffusion is reduced by the wall, which is consistent with the measured Debye length.

The presence of a rigid wall at \( z = 0 \) adds a repulsive electrostatic force along \( z \). The temporal linearity of the MSD is not altered by the presence of the wall, except for the vertical diffusion \( z \). The vertical diffusion is reduced by the wall, which is consistent with the measured Debye length. Further including sedimentation restricts the validity of the previous result along \( z \).

The presence of a rigid wall at \( z = 0 \) adds a repulsive electrostatic force along \( z \). The temporal linearity of the MSD is not altered by the presence of the wall, except for the vertical diffusion \( z \). The vertical diffusion is reduced by the wall, which is consistent with the measured Debye length.

The presence of a rigid wall at \( z = 0 \) adds a repulsive electrostatic force along \( z \). The temporal linearity of the MSD is not altered by the presence of the wall, except for the vertical diffusion \( z \). The vertical diffusion is reduced by the wall, which is consistent with the measured Debye length. Further including sedimentation restricts the validity of the previous result along \( z \).
allowed us to infer the local diffusion coefficients $D_i(z)$, down to $z = 10$ nm, as shown in Fig. 1a). The results are in excellent agreement with the theoretical predictions, $D_i(z) = D_0 \eta/\eta(z)$ and $D_z(z) = D_0 \eta/\eta_z(z)$, using the effective viscosities of Eqs. (3) and (4), thus validating the method.

So far, through Figs. 1a), 3b) and 4, we have successively presented the various measured statistical quantities of interest, as well as their fits to corresponding theoretical models. Therein, we essentially have three free physical parameters, $B$, $\ell_B$, $\ell_D$, describing the particle and its environment, as well as the a priori undetermined location of the $z = 0$ origin. These four parameters are actually redundant among the various theoretical models. Therefore, in order to measure them accurately, we in fact perform all the fits simultaneously, using a Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm that is well suited for unconstrained nonlinear optimization [34]. To do so, we construct a global minimizer:

$$\chi^2 = \sum_{n=1}^{N} \chi_n^2$$,

where we introduce the minimizer $\chi_n^2$ of each set $n$ among the $N$ sets of data, defined as:

$$\chi_n^2 = \sum_{i=1}^{M_n} \frac{[y_{ni} - f_n(x_{ni}, b)]^2}{f_n(x_{ni}, b)^2}$$,

with $\{x_{ni}, y_{ni}\}$ the experimental data of set $n$, $M_n$ the number of experimental data points for set $n$, $f_n$ the model for set $n$, and $b = (b_1, b_2, ..., b_p)$ the $p$ free parameters. In our case, $p = 4$, and $\{x_{ni}, y_{ni}\}$ represent all the experimental data shown in Figs. 1a), 3b) and 4.

Due to strong dependence of the normal diffusion coefficient $D_z$ with $z$, it is possible to find the wall position with a 10-nm resolution, thus overcoming a drawback of the Lorenz-Mie technique which only provides the axial distance relative to the focus of the objective lens. Besides, the three physical parameters globally extracted from the multifitting procedure are: $B = 4.8 \pm 0.6$, $\ell_D = 21 \pm 1$ nm, and $\ell_B = 530 \pm 2$ nm. Using the particle radius $a = 1.518 \pm 0.006 \mu$m calibrated from the preliminary fits of the interference patterns to the Lorenz-Mie scattering function (see Figs. 2c,d)), and the 1050 kg.m$^{-3}$ tabulated bulk density of polystyrene, we would have expected $\ell_B = 559$ nm instead, which corresponds to less than 2% error, and might be attributed to nanometric offsets, such as e.g. the particle and/or wall rugosities.

Finally, we investigate the total conservative force $F_z(z)$ acting on the particle along $z$. By averaging the overdamped Langevin equation over a fine-enough $z$-binning grid and short enough time interval $\Delta t$, one gets in the Itô convention (corresponding to our definition of $\Delta z$):

$$F_z(z) = 6\pi \eta_z(z) a \frac{(\Delta z)}{\Delta t} - k_B T \frac{D'_z(z)}{D_z(z)}$$,

where the last term corresponds to the additional contribution due to the non-trivial integration of the multiplicative noise [19, 35–37], with the prime denoting the derivative with respect to $z$. From the averaged measured vertical drifts $\langle \Delta z \rangle$, and invoking Eq. (4), one can reconstruct $F_z(z)$ from Eq. (11), as shown in Fig. 1b). We stress that the statistical error on the force measurement is comparable to the thermal-noise limit [38]:

$$\Delta F = \sqrt{24 \pi k_B T \eta_z(z)} a / \tau_{\text{box}}(z)$$,

where $\tau_{\text{box}}(z)$ is the total time spent by the particle in the corresponding box of the $z$-binning grid. To corroborate these measurements, we invoke Eq. (1) and express the total conservative force $F_z(z) = -U'(z)$ acting on the
particle along $z$:

$$F_z(z) = k_B T \left( \frac{B}{\ell_D} e^{-\frac{z}{\ell_B}} - \frac{1}{k_B} \right). \quad (13)$$

Using the physical parameters extracted from the above multifitting procedure, we plot Eq. (13) in Fig. 1b). The agreement with the data is excellent, thus showing the robustness of the force measurement. In particular, we can measure forces down to a distance of 40 nm from the surface. Besides, far from the wall, we are able to resolve the actual buoyant weight $F_g = -7 \pm 4$ fN of the particle. This demonstrates that we reach the femtoNewton resolution, and that this resolution is solely limited by thermal noise.

To conclude, we have successfully built a multi-scale statistical analysis for the problem of freely diffusing individual colloids near a rigid wall. Combining the equilibrium distribution in position, time-dependent non-Gaussian statistics for the spatial displacements, a novel method to infer local diffusion coefficients, and a multifitting procedure, allowed us to reduce drastically the measurement uncertainties and reach the nanoscale and thermal-noise-limited femtoNewton spatial and force resolutions, respectively. The ability to measure tiny surface forces, locally, and at equilibrium, as well the possible extension of the method to non-conservative forces and out-of-equilibrium settings [39, 40], opens fascinating perspectives for nanophysics and biophysics.

We thank Elodie Millan, Louis Bellando de Castro, Julien Burgin, Bernard Trégon, Abdelhamid Maali, David Dean and Mathias Perrin for interesting discussions. We acknowledge funding from the Bordeaux IdEx program - LAPHIA (ANR-10IDEX-03-02), Arts et Science (Sonotact 2017-2018) and Région Nouvelle Aquitaine (2018-IR50304).

\* thomas.salez@u-bordeaux.fr
\! yacine.amarouchene@u-bordeaux.fr

[1] A. Einstein. Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen. Annalen der Physik, vol. 4, t. 17, 1905.

[2] J. Perrin. Les Atomes. CNRS Editions, 2014. Google-Books-ID: A0tBQAQAAQBAJ.

[3] B. U. Felderhof. Effect of the wall on the velocity autocorrelation function and long-time tail of brownian motion. The Journal of Physical Chemistry B, 109(45):21406–21412, 2005. PMID: 16853777.

[4] B. Wang, S. M. Anthony, S. C. Bae, and S. Granick. Anomalous yet Brownian. Proceedings of the National Academy of Sciences, 106(36):15160–15164, 2009.

[5] A. V. Chechkin, F. Seno, R. Metzler, and I. M. Sokolov. Brownian yet Non-Gaussian Diffusion: From Superstatistics to Subordination of Diffusing Diffusivities. Physical Review X, 7(2):021002, 2017.
