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CROSS-CORRELATIONS IN THE BROWNIAN MOTION OF COLLOIDAL NANOPARTICLES

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ABSTRACT The two-body cross-correlation for the diffusive motion of colloidal nano-spheres is experimentally investigated. Polystyrene nano-spheres were used in a very low concentration suspension in order to minimize the three- or more body collective effects. Beside the generally used longitudinal and transverse component correlations we investigate also the Pearson correlation in the magnitude of the displacements. In agreement with previous studies we find that the longitudinal and transverse component correlations decay as a function of the inter-particle distance following a power-law trend with an exponent around -2. The Pearson correlation in the magnitude of the displacements decay also as a power-law with an exponent around -1.

Keywords: *colloidal particles, Brownian motion, cross-correlation.*

INTRODUCTION

In the last two decades, the dynamical behaviour of colloidal particles in the neighbourhood of an interface was frequently investigated [1]. The reason for the growing interest in such phenomena is that they might help in providing a better modelling framework for solving interesting problems such as 2D crystallization, crystal sublimation, interactions between similarly charged particles, Brownian dynamics at liquid interfaces and others [1-3].

Analysis of the Brownian dynamics in such restricted topologies allows also the investigation of more exotic diffusional processes with non-trivial scaling properties [4] and/or the micro-rheology of the fluid [2]. Differences from the motion of simple uncorrelated Brownian particles and consequently the presence of

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some flow-mediated interactions are best revealed by means of well-constructed cross-correlated diffusion coefficients. Surprisingly, the involved correlations are long-ranged, decaying with the distance as a power-law with exponent -2. Their presence was explained in a simple manner by the two-dimensional dipolar form of the flow induced by the colloidal particles [3].

Colloids at the microscopic level were studied experimentally by means of digital video microscopy [5] and optical tweezers [6, 7]. Studies were conceived in different geometries: near a single wall [8, 9], between two walls (see for example [10] and references within), in a quasi-one-dimensional channel [11] or in a small container [12 and references within]. Colloids in confined spaces were also studied by Low Reynolds number simulations [13, 14] and a dynamic density functional theory [15]. Cui et al. [3] used digital video microscopy to demonstrate the drastic difference between the hydrodynamic interactions in a quasi-2D suspension both in a less confined and for a more confined system. Dufresne et al. [9] combined optical tweezer manipulation and digital video microscopy to investigate the diffusion of two colloidal spheres near a flat plate. The study demonstrates that even at large separations a confining surface can influence the colloidal dynamics.

The aim of the present study is to demonstrate once again the presence of the long-ranged correlation between the Brownian particles' displacements and estimate the exponent for the fat-tail. The novelty is, that besides the generally used cross-correlations in the perpendicular and parallel displacements, we measure also the cross-correlation for the scalar displacement of the particles and show that this has also a power-law decay.

EXPERIMENTAL SETUP AND METHOD

To study the phenomena, we used a method similar to the one described in the work of Greczyło et al. [16]. Controlled size polystyrene nano-spheres were dissolved in distilled water. The movement of the particles was recorded using an optical microscope with CCD camera connected to a laptop computer.

The system was prepared in the following manner: the polystyrene nano-spheres were suspended in distilled water. One drop of this suspension was placed on a silica glass slide and covered with a cover slip. By this way a quasi-two-dimensional geometry was achieved. Different sized nano-spheres were used, and for the same size several different experiments were considered. We used suspensions with low nanosphere concentration, in order to minimize three- or more body effects. We performed studies on nano-sphere suspensions with particle sizes: 607 nm, 1.5 µm and 2 µm.

In order to allow a HD resolution for the recordings, the frame-rate of the CCD camera was set to 15 frame/s. As an example, one recorded frame in case of the 2 µm nanoparticles is shown in Fig. 1. We performed quite long recordings, with total frame number of the order of 10^4 frames.

Tracking of the particles was done by a program written in Python. This tracking program uses a python package called *trackpy* [17] that extracts all the necessary information for an advanced statistical investigation of the particles dynamics. The program subtracts also any possible global drift flow. Such a global drift motion would lead to unrealistic correlations in the particles dynamics. Since the particle sizes were uniform in size up to 5%, we were primarily interested to track the *x* and *y* coordinates of each particle on each frame. As an example, a part of the data extracted by the program is shown in Table 1.

First, we have studied the generally used two particle cross correlations (covariance) for the longitudinal and transverse displacements.

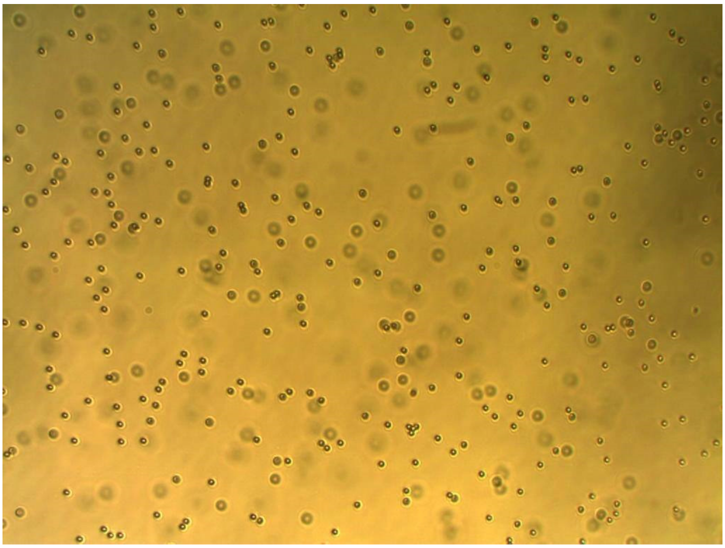

Fig. 1. *Image obtained under the microscope in case of the 2 µm nanoparticles.*

The z_q^{hk} covariance between particles *h* and *k* displacement is determined as

$$z_q^{hk} = \Delta r_q^k \Delta r_q^h, \tag{1}$$

where *q* can be ∥ or ⊥, and the involved parallel and perpendicular displacements $\Delta r_{\parallel}^k$ and $\Delta r_{\perp}^k$ is sketched in Fig.2.

Table 1. Example for the data generated by the tracking program.

Data generated by the tracking program			
y	522.395	378.6569	174.9081
x	738.9558	76.9198	657.3284
mass	428.4899	404.0146	397.8096
size	3.1138	2.6762	3.0369
frame	0	0	0
particle	1	11	14

The time step considered for the displacements is the time-interval between the frames: 1/15 s ≈ 66.7 ms.

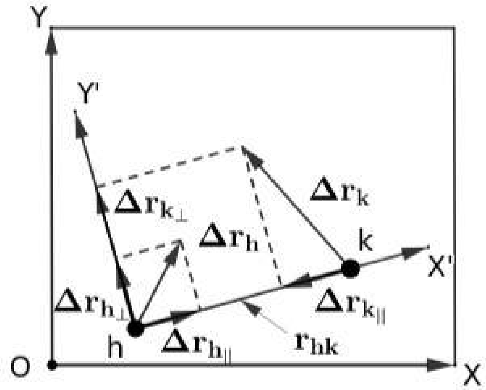

Fig. 2. *Graphical representation of the parallel and perpendicular displacements relative to the direction connecting the two particles.*

The particles in our setup have a spherical geometry, and their diameter has a relative difference less than 5%. Due to the relatively small density, by neglecting the three or more body effects, we expect that the magnitude of this covariance is influenced only by the inter-particle distance $s = r_{kh}$. In order to determine the decay of this covariance as a function of the inter-particle distance we average on all pairs of particles on all consecutive frames where it is found an inter-particle distance: $r_{kh} \in [s - \Delta, s + \Delta]$:

$$z_q(s) = \langle \Delta r_q^k \Delta r_q^h \rangle_{\{k,h | r_{kh} \in [s-\Delta, s+\Delta]\}} \tag{2}$$

Here the value of Δ is suitable chosen so that we remain with enough bins and also there are many (more than 1000) occurrences in each bin. Earlier studies [1] suggested that in a quasi 2D topology the covariance $z_q(s)$ decay as a function of s in form of a power-law with exponent close to -2.

In the present study, we consider yet another correlation ($z_{|\Delta r|}$), dealing with the magnitude of the particles displacements. This cross-correlation is determined by the simple Pearson correlation coefficient [18] defined as:

$$z_{|\Delta r|}(s) = \frac{< |\Delta r_k||\Delta r_h| >_n - < |\Delta r_k| >_n < |\Delta r_h| >_n}{\sigma_n(|\Delta r_k|)\sigma_n(|\Delta r_h|)} \tag{3}$$

where n indicates the same averaging that was considered for $z_q(s)$,
i.e. $n \equiv r_{kh} \in [s - \Delta, s + \Delta]$

EXPERIMENTAL RESULTS

The amount of processed data (number of frames and detected number of particles) are summarized in Table 2. For a given nanosphere size we have combined the data for all the performed experiments in order to obtain a final scaling with improved statistics. The obtained results for the scaling exponents and for the R^2 correlation coefficient is given in Table 3. The results are in good agreement with the ones recently published in [1].

Table 2. The amount of the processed data: the number of frames and detected particles.

Experiments			
Experiment	Part. diam.	No. of frames	Tot. no. of part.
1	607 nm	8000	18314
2	607 nm	12506	40635
3	607 nm	7498	23550
4	607 nm	8000	26464
5	607 nm	8000	22111
6	1.5 µm	7498	7392
7	1.5 µm	6288	4946
8	2.0 µm	2328	19223
9	2.0 µm	2240	19981
10	2.0 µm	8500	19088
11	2.0 µm	3524	2082
12	2.0 µm	14429	8877
13	2.0 µm	14843	8027

In order to illustrate the power-law decay of $z_q(s)$ we present it on log-log scales in case of the 1.5 µm-sized particles. On Fig.3 we plot the results for the longitudinal components and on Fig.4 for the transverse components. In studying the perpendicular and transverse covariance (2) we have chosen the size of the bins as $2\Delta = 2\ \mu m$ and $2\Delta = 3\ \mu m$, respectively. For studying the correlation between the particles displacements (3) the bin size was chosen as $2\Delta = 2\ \mu m$ and the obtained trend for $z_{|\Delta r|}$ is plotted in Fig.5.

In all cases the correlation was detectable until a reasonable large s inter-particle distance of around 50 µm. We obtained similar results for the covariance in the case of 607 nm- and 2 µm-sized particles (see Table 3).

The Pearson correlation coefficient (3) as a function of the inter-particle separation distance exhibits also a power-law trend with a scaling exponent very close to -1. The statistics of the data and the obtained scaling exponents are summarized in Table 4.

Table 3. The statistics of the processed data and results for the longitudinal and transverse covariance (2).

Longitudinal covariance				
Part. diam.	No. of frames	Tot. no. of part.	Scaling exponent	R^2
607 nm	28004	82499	-1.940	0.876
1.5 µm	13786	12338	-2.061	0.970
2.0 µm	43624	57297	-1.940	0.856
Transverse covariance				
Part. diam.	No. of frames	Tot. no. of part.	Scaling exponent	R^2
607 nm	28004	82499	-1.583	0.786
1.5 µm	13786	12338	-2.004	0.962
2.0 µm	43624	57297	-2.137	0.689

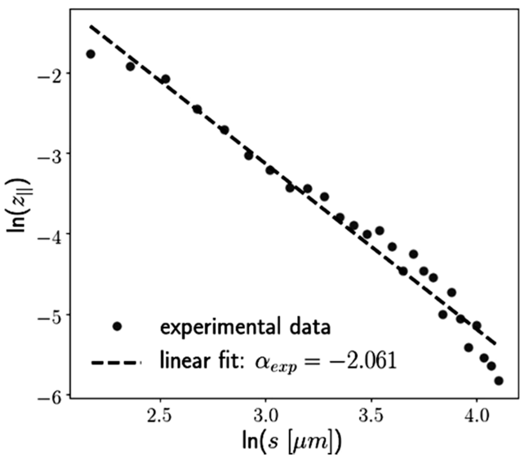

Fig. 3. *The covariance for the longitudinal displacement as a function of the interparticule distance (s) in case of the 1.5 µm-sized particles.*

Table 4. The statistics of the processed data and results for the Pearson correlation between the particles displacement.

Pearson correlation				
Part. diam.	No. of frames	Tot. no. of part.	Scaling exponent	R^2
607 nm	16000	48575	-0.756	0.796
1.5 μm	13786	12338	-0.998	0.926
2.0 μm	13068	58292	-0.639	0.712

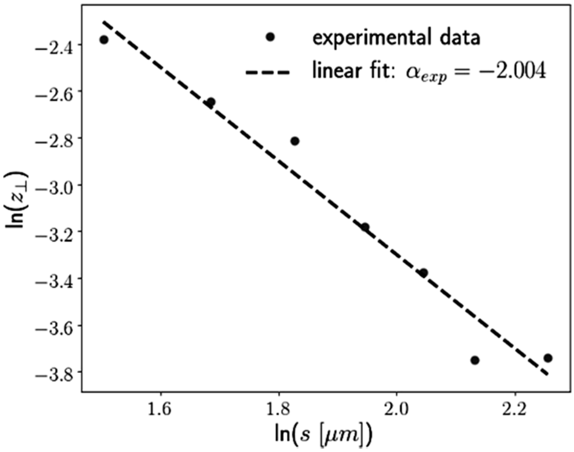

Fig. 4. *The covariance for the transverse displacement components as a function of the interparticule distance (s) in case of the 1.5 μm-sized particles.*

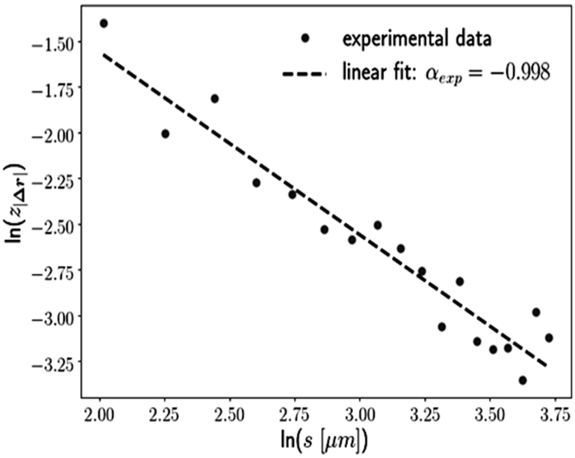

Fig. 5. *The Pearson correlation for the magnitude of the displacements as a function of interparticule distance (s) in case of the 1.5 μm-sized particles.*

CONCLUSIONS AND DISCUSSION

We confirmed that the Brownian like motion of colloidal nanoparticles restricted to a quasi 2D geometry exhibits two-particle cross-correlation decaying as a power-law. For the covariance of the longitudinal and transverse displacements we got a decay exponent similar to the one suggested by earlier studies, close to the value of -2 (Table 3). We have shown that the magnitude of the particles displacements is also correlated, and the Pearson type correlation decays with the interparticle separation distance much slower, as a power-law with an exponent very close to -1. In case of the longitudinal and transverse correlations the values of the exponents are in good agreement with the prediction of a simple hydrodynamic argument [3]. The statistics for the goodness of the power-law fit indicated the largest R^2 value for the experiments performed with the 1.5 μm sized particles. The lowest R^2 values were around 0.7, and were obtained for the experiments performed with the 2 μm size nanospheres.

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