Colloidal dynamics in flow and confinement

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Abstract

The aim of this thesis is to understand how the diffusive and flow behaviors of colloidal hard spheres are influenced by the confinement of nearby walls. The Brownian motion of hard spheres in quiescent bulk fluids is well known, but the presence of confining walls generate new physical phenomena which are still incompletely understood. This situation applies already to the case of confinement by a single wall. In the dilute limit, the diffusion is known to slow down and become anisotropic as the wall is approached. Much less is known about the behavior in more concentrated suspensions. In this regime, hydrodynamic interactions between the particles become more important. They are modified by the structure in the fluid, which itself is also modified by the presence of the wall. Introduction of a second wall, or curved walls gives rise to further changes. All these effects are of relevance for practical problems where colloids occur inside (e.g. cylindrical) capillaries. Turning on the flow, e.g. in a micro channel, introduces additional elements. The inherent shear gradients that are set up, will increase the particle collision rate, and can change the fluid structure as well, in particular if the flow rate (i.e. Peclet number) becomes large. Locally, also direct effects of flow past a wall may occur; e.g. slip, which is related to the particle-wall interaction. The modified diffusion and flow near the wall can have significant implications for the transport of suspensions through capillaries.

To quantify the diffusion and flow of colloids in micro channels, we first developed an improved method for identifying particle trajectories from confocal microscopy images, and subsequently making a clean separation between the advective and diffusive motions. Existing methods for particle tracking in flow did not always produce satisfactory results in terms of spatially resolved diffusion coefficients especially for dilute suspensions and high shear gradients. Our method, which takes the time-dependent particle coordinates as the starting point, was validated for a variety of conditions with computer simulations for Brownian motion superimposed to parabolic flow profiles.

This method was used for analysis of all subsequent measurements in flow. (Intrinsic) particle diffusion coefficients measured after removing the affine motion (including effects of Taylor dispersion), were found to show a strong spatial dependence along the channel cross-section, especially at high particle concentration and high flow rate. For very dilute suspensions the intrinsic

diffusivity did not change, (except very close to the channel walls), in line with expectations. These findings can be attributed to shear induced collisions. Another remarkable observation is that this shear-induced enhancement of the diffusion is strongly counteracted by the contribution from the wall. As a result the diffusion coefficients become very small near the wall even though the shear rate is highest there.

Apparent slip in suspensions has been widely studied, but mostly for non-Brownian particles at very high concentration. Using particle tracking experiments to measure flow profiles, we examined this phenomenon for colloidal suspensions at intermediate concentrations. Use of a simple model that assumes a local depletion of particles very close to the wall, resulted in a remarkably good description of the experiments.

Finally we addressed the diffusive dynamics of colloids confined by cylinders. Varying the cylinder radius from large to small allowed us to examine the local effect of a single curved wall, as well as the global effect of the entire cylinder. Increasing the particle concentration, we found that the local effect of the wall on the diffusive behaviour became less strong. In contrast the effect of the global confinement increased strongly with the concentration, in line with the trend of confinement induced freezing. Analysis of the structure in the fluid revealed that stronger confinement (a smaller confining length) increases the ordering in the system, somewhat similar to the effect of increasing particle concentration. In contrast to dilute suspensions, dense suspensions show anti-correlated diffusion dynamics with local number density with a strong directionality.

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Chapter 1

1 Introduction

Main focus of this introductory chapter is to provide a brief description about colloids, their diffusive behavior and our current understanding of colloidal dynamics in presence of external fields. Colloidal suspensions generally comprise solid particles, with a size ranging from 1nm to 10 μ m, suspended in a liquid medium. In fundamental research, colloids are often used as model systems to help understanding the structure and dynamics in molecular systems. Besides that, colloids also show their own particular behaviors, due to the rich variety of particle interactions they display, and the possible role of hydrodynamic interactions as transmitted via the molecular solvent. Knowledge about the microscopic aspects of structure and dynamics will ultimately help to understand macroscopic behaviors like phase diagrams, relaxation times and rheological behavior. It is also possible to engineer new materials or develop new techniques by studying the dynamics of colloids in extreme environments which can be implemented to solve real life problems.

One way to broaden our understanding of (soft) colloidal materials both in equilibrium and far away from it, is to study their structure and dynamics in real time and space (using optical microscopy). Accurate localization of the (time dependent) locations of individual particles allows to characterize structure (e.g. ordering) as well as the particle dynamics, which can be diffusive and/or advective.

The motivation of this thesis work is, to get a better understanding of the influence of confining walls and shear flow on the dynamics of colloids, considering both their (stochastic) Brownian motion and their (organized) advective motion.

In this chapter the concepts of Brownian motion, diffusive time scales and shear induced diffusion will be introduced briefly. Also the current state of the art in understanding effects of spatial confinements on colloidal dynamics will be summarized. In the last section of this chapter, an outlook will be given on the different research directions that were chosen for extending the current insights.

1.1 General background

The omnipresence of colloidal suspensions in nature as well as in industrial applications has generated a long standing interest amongst scientists to understand the phase behavior and mechanical properties of these complex fluids. Conventionally, suspensions are used in material transport from food industry to oil production and rigorously used to manufacture new products, like pharmaceuticals, food products, paints, cosmetics, etc. heavily used by us in daily life. Colloidal suspensions are here defined as insoluble colloidal particles, suspended in a fluid medium. Unlike solutions where the solute is inseparably mixed with solvent, resulting in a single phase, a suspension is a molecularly heterogeneous mixture in which solid material is microscopically dispersed in a continuous fluid medium. The inherent thermal motion of the colloids plays a crucial role in defining the properties of the suspension: an equilibrium state can often be defined, and systems taken out of equilibrium tend to relax back to this state via the thermally driven motions. By quantifying the motion of colloidal particles in simple liquids (e.g. polystyrene spheres in water), material properties like density, viscosity can be measured. Gravitational forces can in principle play a role, and as such can also contribute to particle motion.

A well-known model system for colloidal suspensions is the hard-sphere (HS) system. The phase behavior of this system is solely determined by the particle volume fraction (Φ)[1]. In HS systems, particles do not interact beyond their radius (a) and the interaction is infinitely repulsive upon contact. The pair potential for monodisperse HS is given by[2],

$$V_{HS}(r) = \begin{cases} 0, & r > 2a \\ \infty, & r \leq 2a \end{cases} \quad (1.1)$$

Owing to the simple nature of the HS interaction, it has been used intensively in many experiments and simulations to understand their phase behavior, glass transition, and relaxation dynamics in bulk as well as in confined systems. Studies on HS systems were mainly focused on the macroscopic level, their phase behavior and rheological properties were the main ingredients to study. It was largely because of industrial applications and partly due to the lack of instrumentation to inspect colloidal dynamics at the microscopic level $O(\mu\text{m})$. In the second half of twentieth century, development of advanced optical methods such as optical microscopy[3], light scattering[4], nuclear magnetic resonance (NMR) imaging [5, 6], confocal microscopy[1, 7], laser-Doppler techniques[8], attenuated total

1.1 General background

reflection infrared spectroscopy (ATR-IR)[9], etc. led us to inspect also the microscopic behavior of (HS and other) colloids in detail. Using dynamics light scattering (DLS) technique [10, 11], it has also been observed how the motion of nano-particles slows down in nano-pores which depends on the particle to pore size ratios.

While these microscopic experiments have produced many new insights on colloidal HS, still there are lots of studies can be done which might improve our understanding about the dynamics of colloids. Some might even argue that everything is known about bulk HS fluids in equilibrium, the application of external constraints such as flow fields or spatial confinements, still invokes behaviors that are not completely understood, and which are of relevance to practical situations. For this reason, colloidal HS are still attractive as a model system. An example is the use of colloidal suspensions in microfluidic chips. With the emergence of microfluidics in the early 2000s it has become possible to mimic and study a wide variety of flow problems (e.g. chromatography, filtration, pore clogging) using specifically designed microscopic geometries. Two aspects are then of general relevance: inhomogeneity of the shear flow, and the effects of proximity to walls.

Spatial non-uniformity of the shear flow changes the picture of shear induced diffusion. In the past decades, this phenomenon has received a considerable attention but mostly for non-Brownian suspensions [12-17]. Much less emphasis was given to shear induced diffusion of colloidal particles so far. In the flow of colloidal particles, advection becomes coupled with Brownian motion, which requires some effort to decouple them before measuring diffusion coefficients. The situation becomes even more complex in case of pressure driven (Poiseuille like) flow, as compared to parallel-plate or Couette flow.

Two other interesting phenomena can play a role in the flow of colloids through a microchannel: (1) the effect of the wall on the Brownian motion and (2) the presence of a solvent-rich film near the wall. Presence of a wall always hinders particle motion because of strong hydrodynamic resistance which results in slower dynamics of colloids. On the other hand, shear force enhances diffusivity. The competing effect of these two opposing factors makes it interesting to examine diffusion near a flat wall in a flowing systems. The presence of a solvent film near the wall will, under flow conditions, create a large velocity gradient as compared to the rest of the fluid, resulting in apparent slip. The occurrence of such apparent slip

is expected to depend on the particle concentration, but a quantification of the effect has not been made for colloidal HS; and hence the implications for the transport of colloidal HS through microchannels are also unknown.

Even in absence of flow, the diffusive dynamics of colloids can pose new cases where the existing knowledge falls short. This is the case for suspensions that are confined by specific geometries. From existing studies, mostly involving confinement between (almost) flat walls it has been found that the diffusive motion can be very different from the behavior of the same particles in the bulk fluid. Both global and local effects of confinement have been found to drastically reduce the amplitude of the thermally driven particle motion, and (hard sphere) systems were found to reach a glassy state at lower concentration than in bulk [2, 18-22]. Reduction of particle diffusivity occurs already due to the restrictions imposed by a single confining wall. Most of the cases explored so far involve colloids near a flat wall [23-25], between two (quasi-) parallel plates [19, 22, 26] or inside a converging micro-capillary nozzle [27]. Understanding of colloidal dynamics in narrow confinement may help to understand ordering of liquid in nano-confined systems and might be inferred to the dynamics at molecular level.

1.2 Brownian motion

Brownian motion is very relevant in the context of this thesis as all the experiments were performed with (nearly) hard sphere colloidal suspensions. This phenomenon is therefore discussed briefly in this section. Brownian motion is the random motion of small particles in a liquid medium that originates from the thermal fluctuations of solvent molecules. In spite of its random nature, it provides a fundamental transport mechanism for colloids. The understanding of colloidal suspensions (or more broadly: soft matter) is intimately connected with Brownian motion. This stochastic motion provides the key concepts in statistical thermodynamics and much of the probability theory is based on Brownian motion[28, 29].

The mechanism behind this stochastic motion lies in the frequent and unrestrained collisions of solvent molecules with the colloid. Averaging these collisions over a timescale that is longer than the inertial relaxation time of the particle, results in a particle displacement with a random magnitude and direction. More precisely, in each of the principal displacement directions, a Gaussian probability distribution

1.3 Diffusive time scales

applies, with a standard deviation that depends on the geometry of the particle and the viscosity of the medium. For particles in simple Newtonian liquids, the random motion is often quantified by mean squared displacement (MSD),

$$\langle \Delta r^2 \rangle = \langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle + \langle \Delta z^2 \rangle = 6D_0 t \quad (1.2)$$

where t is the lagtime, x , y and z indicate the principal directions and D_0 is the diffusion coefficient. This erratic motion was first observed and documented systematically by Robert Brown (named after him) in 1828. Almost 100 years later, Einstein explained this random walk phenomenon successfully in one of his pioneering work [30] (also, Smoluchowski and Sutherland derived this expression separately) by considering the Stokesian expression for the diffusion coefficient,

$$D_0 = \frac{k_B T}{6\pi\eta a} \quad (1.3)$$

where a is the radius of the spherical particle, k_B is the Boltzmann constant, T is the temperature, and η is the solvent viscosity. This is known as free diffusion or self-diffusion of colloids.

1.3 Diffusive time scales

There are two well defined diffusion coefficients based on time scales in colloidal suspensions to characterize Brownian motion: short time self-diffusion, D_0^S and long-time self-diffusivity, D_∞^S [31-33]. For infinite dilution both the diffusion coefficients are same and equal to free diffusion (eq. 1.3). D_0^S provides an estimate of particle motion measured on the time scale (τ) larger than the momentum relaxation time, $\tau_I = m/6\pi\eta a$ (here, m is the mass of a particle), and smaller than the time it requires to diffuse over a distance comparable to its radius, $\tau_B = a^2/D_0$. D_∞^S relates to the particle motion on long time scale, $\tau \gg \tau_B$, which results from the random collision with the solvent molecules and other surrounding particles. In case of long-time self-diffusion, particles move far away from the starting point and exchange places with the neighbouring particles. So, D_∞^S is influenced by the particle motion as well as the dynamic microstructures, however, D_0^S is a time-independent hydrodynamic quantity which depends only on particle mobility [31].

This clear definition of time-scales allows to define the two distinct diffusion coefficients. For very short time scales, $\tau \ll \tau_I$, particle motion continuously slows down due to viscous damping and evolves from ballistic to diffusive regime

[33]. Note that, we measured the dynamics at short time scales presented in this thesis.

1.4 Effect of external fields on colloidal dynamics

Free diffusion of colloids results from the delicate balance between two forces: a thermal force and a viscous drag. This force balance provides a good description of particle transport at microscopic length scales. This mechanism is influenced in presence of external factors, e.g. shear force, concentration gradient, gradient in chemical potential, confinement, etc. In this section, two external parameters are discussed briefly which can influence particle dynamics and closely related to the works presented in this thesis.

1.4.1 Role of confinement

Spatial confinement is known for its tendency to change the viscosity and relaxation time of a suspension, and at a microscopic level the particle motions, sometimes drastically. To understand the transport of suspensions through small geometries, it is essential to know the boundary and size effects imposed by the confining walls on the fluid properties (in equilibrium as well as out of equilibrium). Single walls, two parallel walls [34, 35] or wedge geometries [18, 22, 36] have been used to restrict particle motion in one direction for bi-disperse or polydisperse suspensions in attempts to understand how confinement influences the diffusive dynamics. Confinement promotes glassiness into the systems where the bulk liquid (at the same volume fraction) is still liquid-like. Sometimes suspensions even shows multiple glass transitions upon confinement [18].

1.4.2 Effect of shear flow

Suspensions that are at (or close to) equilibrium generally show an equilibrium structure; at very low volume fractions the (average) concentration will be the same everywhere (except perhaps very close to walls), while at very high volume fractions a crystal like order can be observed. Deviations from this equilibrium structure are repaired through relaxation processes. The characteristic time scale of these processes is tightly related to the so called Brownian or diffusive time, defined as the time required for a particle to diffuse its own radius, $\tau_B = a^2/D_0$. In

1.5 Wall slip in microchannel flow

presence of shear flow, another time scale is also involved, defined by the time required for a particle to move its own radius, via flow. This characteristic time is termed as advective time, $\tau_A = \dot{\gamma}^{-1}$. The combined influence of these two time scales effectively dictates the dynamics of the colloids. The ratio of these time scales are defined as Peclet number (Pe) [7, 37, 38],

$$Pe = \frac{\tau_B}{\tau_A} = \frac{6\pi\eta a^3 \dot{\gamma}}{k_B T} \quad (1.4)$$

with each parameter defined as before. Pe is a dimensionless number which captures the relative importance of each mechanism. For $Pe > 1$ not only the structure of the suspension is altered; also the nature and frequency of interparticle collisions undergoes changes. Particles are increasingly taken along by the flow, which in case of a velocity gradient will generate more frequent collisions. Accordingly, for small Pe (≤ 1) Brownian motion dominates the dynamics whereas for larger Pe (> 1), dynamics is dominated by shear. In the latter case, a new type of diffusion is observed: shear-induced diffusion. This phenomenon was first observed in non-Brownian suspensions [12, 13] where the mechanism was solely flow induced. Note that, for non-colloidal suspensions $Pe \sim \infty$ as there is no contribution from Brownian motion. Near $Pe = 1$, the diffusive dynamics is governed by an interplay of thermal motion and advection [39]. This has not been studied much, but should be of interest for flow of suspensions through pores or microfluidic channels. One possible consequence of shear induced diffusion can be a redistribution of matter, from regions of high shear to regions of low shear [37, 38].

1.5 Wall slip in microchannel flow

Wall slip is often encountered in rheological measurements of non-Newtonian fluids, where it can (sometimes severely) obscure the measurement of the true mechanical properties of the material. Its effects are generally strongest if the viscosity of the fluid is much larger than that of the solvent. In particulate suspensions, slip occurs due to the formation of depleted layer near the wall. Often this slip is termed as apparent slip, to emphasize the mechanistic difference from slip as observed in molecular liquids [40-42]. The so called apparent slip length is quantified by measuring the distance from the wall where the (suitably) extrapolated velocity becomes zero. Mostly Non-Brownian suspensions have been used to study slip [43-47] and findings were explained with shear-induced migration and reduced viscosity near the wall. In case of Brownian suspensions,

less emphasis has been given to the measurements of wall slip. It has been reported that Brownian motion can act against the depletion effect at low shear rates [48] and hence mitigate slip in suspensions. Recent study with glass forming colloidal suspension [49] reported a predominant slip behavior under shear. While at lower particle concentrations the effect may be less dramatic, it can still be of significance, for example for the transport of suspensions through narrow channels, in attempts to measure flow curves via particle tracking velocimetry, or for understanding the local structure of the fluid (and its consequences) very close to the wall.

1.6 Thesis Outline

Based on the brief overview in the previous sections, it is now clear that many key factors are missing from our understanding regarding shear induced diffusion of Brownian particles, wall effect on particle dynamics in flow, depletion effect on apparent slip and the confinement effect of curved interfaces on particle dynamics and structures. In this thesis all those aspects are addressed by performing fairly simple experiments with monodisperse colloidal suspensions and concluded with prominent results.

The thesis is organized as follows. Chapter 2 summarizes the sample preparations and the experimental methods used to study the particle dynamics in confinement as well as in flow. Fabrication methods to design microchannels and microcylinders based on soft-lithography are explained briefly. We then move to the principles of imaging techniques by confocal microscope to record images and address the particle tracking method for data analysis.

A novel method for tracking particles in flow is explained in Chapter 3. Conventional particle tracking methods (as developed for quiescent fluids) do not work anymore if the flow velocity becomes high. Even existing particle tracking methods in flow does not always produce reliable particle trajectories. In this chapter, we present an alternative method to track particles moving in non-uniform flow fields. The novelty of this technique is that it requires only time-dependent particle coordinates to measure velocity profiles, and is fairly easy to implement for dilute as well as dense suspensions. It decouples advection from Brownian motion prior to measurement of the diffusion coefficients. Computer simulations are used to validate the method.

1.6 Thesis Outline

Chapter 4 focusses on how velocity gradients influence the dynamics of colloidal particles in pressure driven flow. We show a clear difference in dynamics between dilute and concentrated suspensions. Results demonstrate that the enhanced diffusion we found, is collision-induced and hence most noticeable in dense suspensions where particles interact more frequently with each other (hydrodynamically in our experiments). We further extend our analysis to capture the shear effect in presence of a flat wall. It is observed that walls always have a diminishing effect on the local diffusion, irrespective of particle concentration. The wall effect dominates over shear effect within 2-3 three particle diameters from the wall.

Owing to the excluded volume interactions between the particles and the wall, the local solids concentration near the wall becomes lower than that in the bulk, causing a local reduction of the suspension viscosity. The length scale of this zone is comparable to particle size. When the flow is set, particle can move easily over a flat wall due to the formation of low viscous thin lubrication layer. This causes apparent slip. In chapter 5, we examine the apparent slip length as a function of particle concentration. The experimental results are compared with a simple model considering particle-wall hard sphere interaction. We find a remarkably good agreement of theoretical and experimental results.

Chapter 6 presents a study on diffusive dynamics of particles confined in (narrow) micro-cylinders. We made successful attempts to investigate particle dynamics as a function of particle volume fraction inside well-defined microcylinders. Our experiments demonstrate that the particle dynamics slows down with the increase in particle concentration or decrease in cylinder radius, somewhat similar to earlier studies with parallel plate geometry, but the confinement effect is drastic and much more eminent in concentrated suspensions. Confinement induces a layering into the system, which becomes prominent with the increase in particle concentration or the reduction in cylinder radius. The peaked structure in the radial direction shows a remarkable anti-correlation with the magnitude of the radial MSD. Motion in azimuthal direction appears to be always larger than that of radial component (independent of local number density). In this chapter, we also demonstrate that, dynamics is diffusive between the layers and sub-diffusive in the layer.

Finally, Chapter 7 summarizes and concludes all the work presented in this thesis with the key findings. Here, we also mention some possible extension of future work which can be performed by using similar systems.

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Chapter 2

2 Materials and methods

This chapter gives an overview of several experimental aspects that are common to all following chapters. This comprises the materials used, covering both the colloidal fluid and the microfluidic chip, and the microscopy technique to view the particle dynamics. First, the basic principles of silica sphere synthesis are mentioned along with the preparation of samples. Next, the fabrication steps for well-defined confining geometries are explained. Following this, we discuss the principles of Confocal Scanning Laser Microscopy (CSLM), with particular attention to technical issues relevant for this thesis work. Also some basic methodical aspects of particle tracking are discussed. Finally, we describe the procedures to locate particles and identify their trajectories from confocal images.

2.1 Particle synthesis and sample preparation

For our experiments we used silica spheres of 1 μm outer diameter (2a) which is a very suitable size for studying the Brownian motion of colloids using optical microscopy techniques. Incorporation of fluorescent molecules in the core enabled visualization of the particles in a confocal fluorescence microscope. We synthesised the spheres in house, based on the methods of Stöber [1] and Van Blaaderen [2, 3]. These methods are now explained briefly.

The synthesis of silica spheres with uniform size was demonstrated by Stober *et.al.*[1] already in 1968. Their method has since then been used by many researchers as a standard procedure for producing monodisperse silica spheres, in the range of 0.05-2 μm diameter. Methanol, ethanol, n-propanol or n-butanol were used as solvents, and tetra-esters of silicic acid as precursor for the silica, while ammonia was used as catalyst. The reaction was started by adding the precursor to the mixture of ammonia and alcohol. The reaction chamber was continuously agitated by a magnetic stirrer to maintain homogeneity, to speed up reactant transport and to keep the formed silica spheres suspended. By changing the alcohol and the concentrations of precursor and catalyst, they could create silica spheres with a tunable size while maintaining a good monodispersity.

As these particles do not contain any dye, they are not optimally suited for fluorescence microscopy. Addition of fluorescent dye in the solvent might be a remedy, producing an image of dark particles in a bright background; however then the image quality would not be very high, the particles could not be localized so accurately and also the particle interactions might be altered by the dye (e.g. through adsorption). A better method is to tag the particles with a fluorescent dye (eg. Fluorescein (FITC) or Rhodamine (RITC) isothiocyanate in the core, as done by Verhaegh and van Blaaderen in the 1990's [2, 3]. They were able to create monodisperse silica spheres with covalently bonded fluorescent molecules in the centre (see Fig.2.1). Major advantages of this method are the homogeneous distribution of dye, the prevention of dye leaching, and the retainment of the silica chemistry at the outer surface of the sphere. In the process, FITC or RITC is first covalently attached to (3-aminopropyl) triethoxysilane (APTES). The coupling product is then added simultaneously with the tetraethyl orthosilicate (TEOS) to an ethanol and ammonium hydroxide medium, just as in the Stöber method. Since the incorporation of the APTES leads to a reduced colloidal stability, a small amount of TEOS is added shortly after completion of the synthesis of the cores. The non-fluorescent shell is then grown by adding TEOS in a seeded growth process.

Fig. 2.1: Schematic of core-shell silica spheres. Dark region in the centre corresponds to the dyed silica and white outer part indicates silica.

We largely followed the method mentioned above to synthesize FITC labelled silica spheres. A specific point of attention was that the radius had to be doubled, meaning that the final particle volume would become 8 times as large. This necessitated dilution steps to avoid reaching very high volume fractions, and the judicious addition of not only TEOS but also extra water (since the reaction consumes water). The TEOS concentration had to be kept low enough to avoid formation of secondary nuclei; therefore it was added in many steps and over a period of 2 weeks. After completion of the synthesis, the particles were transferred to water medium, to increase their long term stability.

SEM images of the cores and the final particles are shown in Fig. 2.2. Fig. 2.2(c) demonstrates a dense layer formed after sedimentation of the silica in water-glycerol solvent. The obtained densely packed crystal-like structure confirms that the particles are almost uniform in size. In Fig. 2.2(d), the radial distribution function $g(r)$ is plotted as a function of normalized distance.

The volume fraction Φ is one of the key variables in our experiments. Even for hard sphere systems, experimental difficulties can affect the accuracy with which it can be measured and hence controlled [4]. For our silica spheres Φ can be calculated under the assumption that the volume of micro-pores which is accessible to solvent, can be neglected. In that case, the mass density of the particles does not change if they are transferred between the dry state and the dispersed state. The mass density ρ_p can then be measured in the dried state and used in $\Phi = q_p c$ with $q_p = 1/\rho_p$ and c the particle weight concentration in the suspension.

Fig. 2.2: Scanning Electron Microscope (SEM) image of samples of silica spheres. (a) Image of the cores, taken immediately after their synthesis (b) Image taken after growing particle size to $1\mu\text{m}$ in diameter. (c) CSLM image of a typical crystal structure of silica sphere in water-glycerol medium. scale bar $=10\mu\text{m}$. (d) Radial distribution function $g(r)$ of the structure presented in (c); $d=2a$.

To measure ρ_p , we prepared a stock solution with an expected volume fraction of ≈ 0.1 . Measuring the mass density of this suspension $\langle \rho \rangle$ as well as the weight fraction w of dry material after evaporating the solvent, then allows to calculate ρ_p by assuming no excess mixing volume:

$$\langle q \rangle = wq_p + (1 - w)q_s \text{ with } \langle q \rangle = 1/\langle \rho \rangle \text{ and } q_s = 1/\rho_s \quad (2.1)$$

Repeating this measurement three times for a stock suspension in water, we found the mass density the silica (ρ_s) to be $1.89 \pm 0.02 \text{ g/ml}$.

The dispersing medium was obtained by mixing water and glycerol in a 1:4 weight ratio. At this composition, the refractive index is close to that of the silica (≈ 1.45); this allowed us to observe particles through an optical path of $\approx 20 \mu\text{m}$, even in

2.2 Microchannel and microcylinder fabrication

concentrated systems. The mass density of the solvent mixture is $\approx 1.20\text{g/ml}$ while the viscosity η is $\approx 60\text{mPa.s}$. Due to the mass density mismatch $\Delta\rho$ between the silica and the solvent, sedimentation of the particles is not rigorously prevented. However the relatively large solvent viscosity helps to mitigate the effect. Calculating the terminal sedimentation velocity v_t for an isolated particle:

$$V_t = \frac{2\Delta\rho g a^2}{9\eta} \quad (2.2)$$

with g the acceleration due to gravity (9.81 m/s^2), we find 6.3 nm/s . The real speed becomes even smaller in concentrated suspensions as well as in flow. Most of our experimental time scales are in the range of $150\text{-}500\text{s}$ while most volume fractions $\Phi > 0.1$. Hence the depletion of particles from the uppermost part of our (confined) suspensions due to gravity should not involve more than $1\text{-}2\text{ }\mu\text{m}$, which is a small fraction of the typical $24\text{ }\mu\text{m}$ height of our channels.

Transfer of the solvent from pure water to the glycerol-water mixture was achieved by four times repeated centrifugation (at $\approx 1000\text{ g}$) and resuspension, ultimately leading to a stock dispersion of $\Phi = 0.49$. Suspensions at different particle volume fractions were prepared by adding the required amount of water-glycerol. We also added LiCl salt up to 0.8 mM , to screen the surface charge. The corresponding calculated electrical double layer thickness is 8 nm [5]. This should ensure that the electrostatic repulsion force is sufficiently short-ranged make a nearly HS system in water-glycerol mixture, while still maintaining colloidal stability.

2.2 Microchannel and microcylinder fabrication

Experiments were performed either in straight microchannels with smooth walls, or inside microcylinders embedded in the side of a microchannel. Here we briefly discuss the technique to manufacture them. Soft lithography (a low-cost method) [6] is used for the formation and manufacturing of micro- or nano structures. Conventionally, in this process an elastomeric stamp with patterned relief structures on its surface is used to transfer these structures to another substrate. Here the feature size can range from 30 nm to $100\text{ }\mu\text{m}$. Depending on the required resolution, the stamp is produced by standard photolithography or electron-beam lithography, shown in fig. 2.3(a).

The required design on the stamp is developed on a disk-shaped silicon wafer (diameter = 4 inch), coated beforehand with SU-8 at the desired layer thickness. SU-8 is an epoxy based ‘negative’ near-UV photoresist originally developed for Microelectromechanical systems (MEMS) and other microelectronic applications. When exposed to UV light, its molecular chains undergo a cross-link reaction, causing the SU-8 to solidify. SU-8 is highly transparent in the ultraviolet range. This allows for the fabrication of relatively thick (hundreds of micrometres) structures with nearly vertical side walls.

Fig. 2.3: A sketch to show the preparation of microchannels. (a) Schematic of photo-lithography. (b) Schematic of soft lithography.

The SU-8 structures (*i.e.* molds) on the silicon wafer are then replicated in poly(dimethyl-siloxane) (PDMS) by negative stamping, shown in Fig. 2.3(b). Prior to the replication, an anti-sticking layer of H,1H,2H,2H-Perfluorododecyltrichlorosilane (FDTS) is deposited on the stamp. Omission of this step leads to incomplete replication. Placing the stamp together with a small amount of FDTS in a desiccator under vacuum creates a saturated FDTS vapour, from which the molecules bind to the stamp. Half an hour was given for this process.

The PDMS we used (Sylgard 184, Dow Corning) is a widely used silicon-based organic polymer, which is particularly known for its favourable rheological (or flow) properties. A mixture of pre-polymer and curing agent (weight ratio 10:1) is prepared in a plastic cup and vigorously stirred to mix those two components

2.2 Microchannel and microcylinder fabrication

homogeneously. Then the cup is placed in a desiccator to degas. After the mixture is completely free of air bubbles, it is poured gently over the SU8 stamp in a petri dish. Finally the PDMS mixture on the mold is cured in an oven at 65 °C for one hour. After curing, the PDMS block is separated from the wafer: the sidewalls and ceiling of the microchannel are already available in this stage.

The two ends of the PDMS channels are then made hollow by punching a precision needle with 1mm inner diameter and removing the separated PDMS inside it. These holes are used subsequently to connect the channels with hydrostatic pressure heads, as needed for the flow control.

Fig. 2.4: Schematic of the microchannel and microcylinders (not drawn to scale). The transparent cuboid structure in each diagram indicates the PDMS block, the circular (Sky Blue) section is the glass cover slip. Two long cylindrical structures at both the ends signify inlet and outlet positions. (a) microchannel with smooth side walls. (b) microcylinders with different inner diameter are embedded at the side of the microchannel.

Finally, the PDMS blocks are bonded onto a 170 μ m thick glass cover slip, shown in Fig.2.4, to close the channel. Fig. 2.4(a) shows the design of a 2 cm long channel with smooth side walls made from PDMS and closed by a glass cover slip. The channels thus contain two PDMS side walls, a PDMS ceiling and a glass bottom. Fig. 2.4(b) shows the design of microcylinders with different cylinder diameters (40, 20, 10 and 5 μ m) connected with the main channel. This design allows to populate the cylinders with suspensions in a simple way.

Prior to bonding, the PDMS and cover slip are cleaned successively with methanol, acetone and isopropanol and then treated with an oxygen plasma for 50 s, using 100W UV light to make them hydrophilic. These steps should ensure a strong bonding without any leakage. Because of the plasma treatment, the channel walls become hydrophilic for a duration of up to 200 hours. While this is ample time to achieve permanent bonding between the PDMS slab and the glass, the hydrophilic nature of the PDMS could lead to (undesirable) sticking of silica particles to the ceiling and sidewalls. Using the fact that PDMS is inherently hydrophobic, we chose to wait for more than two weeks before filling the channels with suspension. The success of this approach was verified by inspection of images recorded by the CSLM.

2.3 Confocal microscopy

Confocal Scanning Laser Microscopy (CSLM) is a well-established technique for studying the structure and dynamics of colloidal suspensions both in equilibrium and away from it, the velocity patterns in flow geometries using colloidal tracers, the formation of ‘coffee rings’ and much more. In this section, an introduction into CSLM is given, supplemented with some specific conditions applicable to experiments for this thesis.

The main principle of CSLM has been very well explained by Minsky [7]. The technique was designed to overcome some limitations of traditional wide-field fluorescence microscopy where the entire sample is illuminated evenly by light, and both in-focus and out-of-focus reflected lights are detected by the camera. This causes a large background contribution and makes it difficult to study small sections of a sample in soft matter systems. In contrast, CSLM is very successful in eliminating out-of-focus signal.

In Figure 2.5(a), the basic principle of a confocal microscope is shown, where a point illumination is used for incident light and a pinhole is kept in an optically conjugate plane in front of the detector. The name "confocal" originated from this configuration. Fig. 2.5(b) shows a conventional point scanning CSLM. Laser light (blue) is guided by the dichroic mirror (high pass filter) towards the scanning mirrors which help to scan the sample in 2D. Light is then reflected and passes through the objective to illuminate the sample. The reflected signal (green) from the

2.3 Confocal microscopy

Fig. 2.5: (a) Schematic of the basic principle of confocal microscopy (not drawn to scale). (b) Schematic diagram of conventional confocal microscope (not drawn to scale). Blue dashed line indicates incident laser beam and green line corresponds to the reflected signal. The rotating mirrors help to scan the sample faster. (c) Confocal image taken at a height of 12 μm from the bottom of a suspension at volume fraction $\Phi = 0.05$; scale bar = 10 μm .

fluorescent molecules then goes back along the same path as the incident light, except that it now passes through the dichroic mirror and goes through a pinhole before reaching the camera. Since the pinhole rejects a large proportion of the out-of-focus light, only the signal from the focal plane is detected by a Charge-Coupled Device (CCD) camera. Thus CSLM provides a way to obtain good quality images with high axial resolution, shown in Fig. 2.5(c). Since the objective is mounted on a piezo, it is possible to scan the sample in 3D along the optical axis. Combining the 2D slice of images along optical axis recorded at very short and regular intervals by the CSLM, 3D image of the sample is constructed [8].

For our experiments, we used two different confocal microscopes: (1) UltraView LCI10 system (Perkin Elmer) containing a Nikon Eclipse inverted microscope and (2) VisiTech's 'VT-infinity³'. The LCI10 is equipped with two rotating discs: one with pinholes and the other one with conjugated microlenses. Light from a 488 nm solid state laser at a typical power of 15 mW is shone on the specimen point by point and the emitted light from the fluorescence is filtered by a dichroic mirror before detection by the Hamamatsu ORCA 12 bit CCD camera. This provides good images but the recording speed (up to ≈ 15 fps) is a limiting factor for experiments in flow. Another limitation of this microscope is the fixed pin hole size (optimized for 60X and 100X magnification) which cannot be controlled to filter more light or allow more light.

These limitations are overcome by using the (more modern) VT-infinity³. Using galvanometers, this system scans the sample in two directions line by line at the same time. The scanning starts from the centre of the illuminated sample and the lines move upward and downward simultaneously which improves the scanning speed and thus it can reach up to 1000 frames/s. The sample is still illuminated with a 488nm laser source, but the power goes up to 100 mW and can be controlled via the software. Another advantage of this instrument is the flexible pinhole size which varies from 10 μ m to 60 μ m and helps to remove more out of focus reflected lights (fig.2.5 (c)). Confocal unit is equipped with 'ORCA-Flash 4.0' camera with high sensitivity results from its high quantum efficiency and low noise. This CSLM is very useful for studying fast and dynamics processes.

2.4 Particle tracking

Particle tracking comprises the localization of particle centres from optical images, and the subsequent construction of particle trajectories from the time-dependent locations. We have used it to track fluorescent colloidal particles in time series of 2D images recorded by CSLM. The basic principles that are widely used to track colloidal particles were developed by Crocker and Grier [9] and later extended by E. Weeks [10]. This method is based on two main assumptions: particles are spherical in shape, thus they appear like a disk in 2D images, and a particle centre corresponds to the maximum brightness of intensity. This technique is very useful to track Brownian motion in a quiescent suspension. We used Interactive Data Language (IDL) software for image processing and data analysis.

2.4.1 Identification of particle trajectories

In the first step, noise is eliminated from the confocal images by spatial filtering to enhance the contrast between the features and the background. Next, each particle centre is located by fitting the intensity profile and considering the (x,y) location where the fitted intensity becomes maximum. Subsequently, the trajectory of each particle is constructed by comparing consecutive frames and maximizing the probability distribution of particle displacement within a certain range [9]. This step labels all locations belong to the same trajectory with a unique identifier. A detailed description can be found in ref. [9, 10].

Proper identification of particle trajectory is one of the main operational step to accurately obtain the diffusivity data. Once the particle centres are located in successive frames, every given co-ordinate is matched with the corresponding location in next images to generate the trajectory in time. One coordinate will be connected with only one location in the preceding and successive frames. This is done by considering the probability distribution of single Brownian particle. According to Brownian dynamics, the probability that a single Brownian particle will move a distance s from its initial position in time t , is given by

$$P(s | t) \propto \exp\left(-\frac{s^2}{4Dt}\right) \quad (2.4)$$

where, D is the free diffusion co-efficient of the particle. Thus, for N number of non-interacting particles in a given region, the probability distribution is

$$P(\{s_i\} | t) \propto \exp\left(-\sum_{i=1}^N \frac{s_i^2}{4Dt}\right) \quad (2.5)$$

and the most likely particle identification in the consecutive frame is the one which maximizes the probability distribution. After performing this step, a track file is generated which contains the information of particle coordinates (x, y in 2D tracking along with z in 3D tracking), intensity, radius of gyration, frame numbers and track numbers. We used these data files for further analysis.

This is a useful method to measure self-diffusion of colloids in soft matter systems without any ambiguity in quiescent suspensions and also widely used. But, in presence of strong lateral motion, further steps are necessary for data analysis which are discussed extensively in Chapter 3.

2.4.2 Drift correction

Generally, mechanical vibration of the microscope table, floor, etc. influence the measurement of particle dynamics which is incorporated through the motion of individual particle. These kind of vibrations are known as mechanical drift and fluctuates over time. It can be important to remove the drift from particle trajectories prior to measure the diffusion coefficients. Drift is detected by measuring the displacement of centre of mass of all the particles over time and is generally separated per co-ordinate.

Fig. 2.6: Drift signal of a bulk suspension at $\Phi = 0.05$ in two different directions, x (red) and y (black).

One typical drift signal is presented in fig. 2.6. It is clear from the plot that the centre of mass of all the particles moves approximately 100nm in x-direction and 25 nm in y-direction within 140s which is significant for slowly moving particles either in confinement or in high viscous medium. This random drift is then subtracted from the time-dependent particle co-ordinates.

2.4.3 Mean squared displacement

A key assumption in particle tracking microrheology is that the thermal motion of colloidal particles reflects the mechanical properties of the surrounding medium. Analysing the statistics of the displacements of an individual particle, or averaging over many particles, it is possible to quantify properties like the viscosity of the surrounding liquid. The stochastic motion is often represented via the so called

2.4 Particle tracking

mean squared displacement (MSD) function. Assuming evenly spaced time steps, the generic expression for the MSD in one direction is,

$$\langle x^2(\tau) \rangle = \langle [x(t + \tau) - x(t)]^2 \rangle \quad (2.6)$$

where $x(t)$ is the particle position along x -direction at real time t , τ is the lag time between two successive steps, and the bracket $\langle \rangle$ indicates a time-average over t

Fig. 2.7: Mean squared displacement, $\text{msd}(\tau)$ vs lagtime (τ) of $1\mu\text{m}$ silica spheres in water-glycerol mixture at room temperature (image shown in fig. 2.5(c)). $\Phi = 0.05$. Blue lines are computed from the time-average of individual trajectory and the red line is the time and ensemble average of all trajectories.

and/or an ensemble-average over all trajectories. Fig.2.7 shows an example of MSD plot. The red line is the ensemble average over all the trajectories, whereas all blue lines correspond to the MSDs of individual trajectories. In a Newtonian fluid, the MSD is related to the diffusion coefficient, $\text{MSD} = 2dD_0\tau$, where D_0 is the diffusion coefficient, and d indicates dimensionality.

2.4.4 Spatial Resolution

The precision of the particle localization can be a limiting factor in the measurement of diffusion coefficients. One way to determine the ‘noise floor’ of the MSD is to measure the displacements of fixed particles glued to a surface. In our case, we glued $1\mu\text{m}$ polystyrene (PS) spheres on a glass cover slip by evaporation a small drop of dilute water-PS dispersion and sintered the particles at

60°C. Particles were imaged by the CSLM at 100X magnification for 5000 frames, after which the MSD was measured. Fig. 2.8 is the typical example of an MSD (red points) of sintered particles over time and the average MSD is $1.36 \times 10^{-4} \mu\text{m}^2/\text{s}$ which corresponds to a displacement resolution of $\approx 12 \text{ nm}$. Ideally speaking, the MSD should be zero as all the particles are fixed on the surface, but any uncorrected drift or error in the localization (e.g. due to fair image quality) will end up as a lagtime independent MSD.

Fig. 2.8: MSD of $1 \mu\text{m}$ polystyrene particles sintered on a glass surface.

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Chapter 3

3 Measuring advection and diffusion of colloids in shear flow

Analysis of the dynamics of colloids in shear flow can be challenging because of the superposition of diffusion and advection. We present a method that separates the two motions, starting from the time-dependent particle coordinates. Restriction of the tracking to flow lanes and subtraction of estimated advective displacements are combined in an iterative scheme that eventually makes the spatial segmentation redundant. Tracking errors due to neglect of lateral diffusion are avoided, while drifts parallel and perpendicular to the flow are eliminated. After explaining the principles of our method, we validate it against both computer simulations and experiments. A critical overall test is provided by the Mean Square Displacement function at high Peclet numbers (up to 50). We demonstrate via simulations how the measurement accuracy depends on diffusion coefficients and flow rates, expressed in units of camera pixels and frames. Also sample-specific issues are addressed: inaccuracies in the velocity profile for dilute suspensions (Volume Fraction ≤ 0.03), and tracking errors for concentrated ones ($VF \geq 0.3$). Analysis of experiments with colloidal spheres flowing through micro channels corroborates these findings, and indicates perspectives for studies on transport, mixing or rheology in microfluidic environments.

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3.1 Introduction

The behavior of colloidal particles in microscopic geometries is of interest for a growing number of applications like their synthesis in droplets [1] or microfluidic channels [2], their use as (bio)sensors in microfluidic chips [3], assembly in confined geometries [4], and transport through capillaries [5, 6] or porous networks [7]. Also from a fundamental point of view these systems are interesting, an important reason being that geometrical confinement can strongly influence both the spatial distribution and the dynamics of the particles [8-12]. The recent emergence of microfluidics has further enhanced this interest by adding shear flow as an additional dimension to the problem. The combination of confinement and spatially varying flow has been addressed at the level of the advective velocity and concentration profiles [5, 6, 13-17]. However data on the diffusive dynamics in flow are scarce, especially for Brownian particles. One reason for this could be the difficulties in analyzing the behavior of particles that show both diffusion and advection.

In the flow of colloidal suspensions, two types of motion are superimposed onto each other. On one hand the particles tend to follow the streamlines of the overall material, but on the other they also deviate from it, due to collisions with either solvent molecules or other particles. From a scientific point of view, both types of motion are of interest. The advective (average) motion as characterized by the flow profile reflects the nonlinear rheological behavior of the material [18-20]. Knowing the driving force (e.g. a pressure drop) and the geometry (e.g. a capillary or a rectangular channel), the measured velocity profile can be either inverted or fitted to a flow curve (e.g. [18]). The deviatoric (stochastic) motions of the colloids contain complementary information. Depending on the fulfilment of certain assumptions about the probe-matrix interactions, they can reveal local viscoelastic properties of the material surrounding the particles [21-27].

However the problem is how to separate the two types of motion from each other (in a video microscopy experiment). The stochastic motion adds ‘noise’ which should be properly ‘averaged out’ before the advective motion can be found. Conversely, the average motion provides a background signal which has to be subtracted before the fluctuations can be quantified. This problem is not exclusive to colloids; it is also encountered in flow of suspensions of much bigger particles [28-30] and dry granular flows [31], where the diffusion is not Brownian but collision-induced. For non-colloidal particles in a homogeneous shear flow, the diffusive dynamics could be extracted using a correlation technique [29, 30, 32].

3.1 Introduction

More recently also flows with gradients in shear have been considered. Besseling et al [33] describe the combination of image correlation and particle tracking to find velocity profiles of concentrated suspensions flowing through micro channels.

In spite of these significant achievements, there are still regimes of relevance for fundamental and applied studies, in which decomposition of the particle motions into advection and diffusion remains challenging. A good example is the case of colloids flowing at high Peclet numbers, where it has been found that concentration gradients can develop as a consequence of shear induced diffusion [5, 6, 34]. However measurements of the diffusion coefficients themselves were not presented for this case. It is clear why these are difficult: the stochastic displacements are relatively very small.

In this paper we present a method that tackles this problem by combining a careful tracking of particle displacements with a precise subtraction of the local advective motion. Tracking erratically moving particles in high speed flow is a well-recognized problem. The standard routine for micro-rheological applications at rest [35] tries to find the new position of each particle in the next video image by searching within a circle. Use of the same method in flow, presents a challenge. In case of directional motion with velocity v detected with a time resolution Δt , the search radius needs to be (at least) $v \times \Delta t$. If this radius becomes so large that other particles are found inside the same circle, ambiguities occur, leading to (very detrimental) misidentifications. Clearly one remedy could be to diminish Δt via the speed of the camera. But regardless of the success of the latter, the desire to ‘stretch’ the range of addressable flow speeds via an improved data analysis will always remain.

One such improvement consists of subtracting the estimated advective displacement prior to the tracking, and applying this in an iterative scheme. This approach has been successfully used but a remaining issue, called ‘accumulated strain’ was identified for high shear flows [33]. Also other (potential) issues of tracking in high shear flows exist, which have not been addressed so far. Scarcity of the particles is a notable one, with implications for the study of dilute systems (e.g. use of the colloids as diffusive tracers). In this regime, accurate measurement of the velocity profile requires an experiment of long duration, which in turn can generate (more prominent) issues with fluctuations in the flow or drift of the microscope table. We will present mitigations to each of these issues.

Regarding the measurement of diffusive behavior, it is important to note that (near) absence of particle misidentifications is required but not necessarily sufficient. Even if the tracking is flawless, the mentioned issues with noise or velocity drifts may cause significant inaccuracies in the apparent diffusive behavior. For this reason we will consider the measured Mean Squared Displacement (MSD) function as the benchmark of our analysis.

After explaining the principles of our method, we will first validate it by comparison to computer simulations in which an isotropic Brownian diffusion is superimposed onto a parabolic flow profile. Tagging of particles is used to quantify the proportion of tracking errors, as a function of particle concentration, flow rate and diffusivity. Additional analysis of the apparent diffusion coefficients a function of these parameters, then allows a certain disentanglement of the contributions of tracking errors and velocity errors to the (in) accuracy of the MSDs. Further, also analysis of experiments in microchannel flow will be presented. Here we will highlight the difference between the analysis at high and low particle concentrations, and demonstrate the effect of corrections for drift.

3.2 Experiments

Rectangular microchannels were fabricated by bonding a PDMS slab containing the side walls and ceiling onto a 170 μm thick glass coverslip. Particle-laden fluids were pumped through by setting a difference in hydrostatic pressure between inlet and outlet (see [36] for details). All suspensions consisted of 1 μm diameter silica spheres with fluorescent cores (see [37, 38] for synthesis and characterization details) dispersed in a refractive-index matching mixture of water and glycerol with a viscosity of ≈ 100 mPa.s. Fluids were prepared at volume fractions ϕ of 0.03 and 0.3.

Fig.3.1: Schematic of the 3D channel geometry and coordinate system with X (horizontal, flow), Y (horizontal, perpendicular to flow) and Z (vertical). Respective dimensions of the channel: 2 cm, 30 μm and 22 μm . Video recordings were taken in (X,Y) planes at $Z = 11$ μm (for reasons of symmetry).

3.2 Experiments

All channels (see Fig. 3.1) had a length of 2 cm, while their (width x height) cross sections were $30 \times 22 \mu\text{m}^2$. One additionally explored channel had a cross section of $55 \times 22 \mu\text{m}^2$. Observations were made at $X=1$ cm, with the channel placed on an inverted microscope (Nikon), with a 100x /oil objective offering a (X,Y) field of view of $87 \times 66 \mu\text{m}^2$. An UltraView Confocal Laser Scanning system (Perkin Elmer) was used to visualize the fluorescent particles. The focal Z-plane was chosen halfway between floor and ceiling to ensure the absence of velocity gradients in the vertical direction. The number of localized particles per image was approximately 130 for $\phi = 0.03$ and 1500 for $\phi = 0.3$, respectively.

Typical movie stills for the suspension at low and high volume fractions are shown in Fig. 3.2. Due to the refractive index matching, particles are well resolved, even at $Z = 11 \mu\text{m}$ and $\phi = 0.3$. Particle localization was performed with the publicly available software written in IDL language [39]. The spatial resolution was approximately 0.1 pixel length, for effective pixels of $135 \times 135 \text{ nm}^2$. Smearing of the intensity profiles (as in [40]) turned out to be modest even at the highest explored flow rate. Movies consisted of 500 frames for $\phi = 0.3$, and 1500 for $\phi = 0.03$. Images were acquired at 15 fps ($\Delta t = 0.067 \text{ s}$). During data analysis we discovered that incidentally (once per 10-20 frames) images had not been stored. These errors were identified via the occurrence of instantaneous flow velocities that were twice as high as most others, and repaired by reassignment of the time array, followed by interpolation of the affected trajectories. In subsequent calculations of MSDs these interpolated data were taken out again.

Fig. 3.2: Typical images of particles flowing through channels at $\phi = 0.03$ (left) and $\phi = 0.3$ (right). The channel width is $30 \mu\text{m}$.

3.3 Simulations

To mimic experimental data, particles were generated and displaced inside a box of 600, 200 and 7 pixels along X, Y and Z respectively. Each particle was modeled as an object of 8×8 (x,y) pixels to allow excluded area interactions, and a mass center at a certain (x,y,z) location to enable tracking. The total area fraction (AF) in the (x,y) plane was set via the number of particle centers N_{pc} in the (x,y) range of the box: $AF \approx (64/1.2 \cdot 10^5) \times N_{pc}$. Before each time step, particles had to be added: initially to fill the box with N_{pc} particles, and in the next steps to make up for particles that had left the box. Particles were introduced one-by-one using uniform random generators for the (x,y,z) coordinates, and were rejected if (x,y) area overlap (at pixel level) occurred with existing ones. In each time step, particles were displaced via diffusive steps in the X, Y and Z directions using a Gaussian random generator with imposed standard deviations σ_x , σ_y and σ_z , plus a advective step in the x-direction using an imposed parabolic velocity profile $v_x(y)$. Disappearance of particles (centers) occurred via (x) flow and/or (x,y,z) diffusion.

A systematic variation was made of the diffusion coefficient and the maximum advective velocity, varying $\sigma_x = \sigma_y = \sigma_z$ from 0.2 to 1.0 pixel, and choosing v_{max} between 0 and 8.0 pixel/frame. This upper limit is already beyond practical values for 8 pixel sized particles (it would give a severely smeared image). Explored area fractions were 0.032, 0.32 and 0.43. To enable direct comparisons, the product of N_{pc} and the number of time steps was kept constant at 10^6 . Data were generated in the matrix format as required by the standard tracking software [39], replacing of one of the unused columns to give each particle-time record a unique identifier.

3.4 Data analysis

In our analysis, particle trajectories are obtained in a coordinate system attached to the laboratory. Relative to this system the microscope table exhibits a (slow) motion. The aim of the measurement is to find the motions of the particles relative to the table. Some of the concepts that we used, like the division into flow-lanes and subtraction of estimated advection prior to tracking, show similarity to those described in an excellent review paper [33]. However, the here presented ‘iterative masking’ method that uses particle coordinates only (Sec. 3.4.1.1-3) is new. Furthermore our approach involves specific choices and details which need to be specified in order to fully appreciate the analysis. Operations will be described both verbally and mathematically to facilitate implementation.

3.4.1 Tracking particle displacements

The procedure starts with localizing all particles in each video frame, as usual in particle tracking microrheology [41, 42]. Taking the list of coordinates and times as input, iterative tracking is used to find the time-averaged velocity profile and the particle trajectories. Thereafter it is possible to correct separately for transients in flow rate and for table drift perpendicular to the flow. Subtraction of the instantaneous advective displacements from the ‘real’ trajectories produces so-called ‘residual’ trajectories, from which MSDs in the X and Y directions are calculated. This procedure is illustrated in Fig. 3.3 and explained in more detail below.

Fig. 3.3: Schematic of the procedure to find the particle trajectories. Dotted arrows indicate optional corrections for different types of drift (see text).

3.4.1.1 Identifying particle displacements

To identify the particle displacements, the standard method for materials in the quiescent state [35] is modified. An iterative procedure is used, in which tracking is initially restricted to Regions of Interest which are aligned along X (see Fig. 3.4). These ROIs will be called Y-bins since they are specific for a certain Y (range). The length of each Y-bin is given by the X-range ($x_{max}-x_{min}$) in which particles are detected, while its width ΔY is defined by the total Y-range and the chosen number of bins N_y :

$$\Delta Y = (y_{max} - y_{min}) / (N_y - 1) \quad (3.1)$$

Particles that remain in the same Y-bin during a time step are then identified by standard tracking [39] within a search radius $\Delta r_{\max}$ corresponding to the maximum allowed displacement:

$$(\Delta x)^2 + (\Delta y)^2 \leq (\Delta r_{\max})^2 \quad (3.2)$$

where Δx and Δy are the distances between a particle at time t_k and a particle (in the same Y-bin) at time t_{k+1} . When dealing with high number densities and large x-displacements, an appropriate combination of ΔY and $\Delta r_{\max}$ has to be chosen for the tracking to be successful. Else the search-area around a given particle at time t_k will be contaminated by other particles at time t_{k+1} due to the advective transport. To avoid the ensuing correlation problem (leading to crashes of the algorithm) the Y-bins have to be chosen narrow, but still wide enough to allow measuring a few displacements. This works because the most probable diffusive displacements in the y-direction are the smallest ones (illustrated in Fig. 3.13).

Fig. 3.4: Cartoon of the first step of the tracking procedure. The box is aligned with the flow direction (X). In the left panel, arrows indicate the local flow velocities. The middle panel shows how the particle configuration changes over a unit time step Δt (mainly due to advection). To find the displacement of the green particle, the tracking algorithm needs a minimum search radius as indicated. Other candidate-particles are filtered out by the judicious masking as shown in the right panel. The non-masked flow-lane is called a Y-bin.

To allow a widening of the bins, and hence a more complete detection of the displacements in the next iteration, use is made of the best available knowledge about the velocity profile. Initial estimates for $v_x(y)$ are used to modify the x -coordinates of the particles at time t_{k+1} before comparing them to the coordinates at time t_k :

$$x'_i(t_{k+1}) = x_i(t_{k+1}) - v_x(y_i(t_k))\Delta t \quad (3.3)$$

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where i labels a particle, Δt is the unit time-step and $v_x(y)$ is interpolated at $y = y_i$. This operation, which ‘biases’ the search towards finding the correct displacements and also allows use of a smaller Δr_{max} , is illustrated in Fig. 3.5. After finding which coordinates (x, y) at time t_k and (x', y') at time t_{k+1} belong to the same particle, the advection correction of the x -coordinates at time t_{k+1} is undone to enable a similar comparison between times t_{k+1} and t_{k+2} . We remark that this ‘pairwise tracking’ is the most rigorous way to remove the affine motion; algorithms that assume an average local velocity over multiple time steps could introduce errors, especially if trajectories are long and/or velocity gradients are large [43]. The obtained first estimate of $v_x(y)$ (see Sec. 3.4.1.2) is then used in the next iteration, and so on.

3.4.1.2 Finding the velocity profile

The advective velocity profile is estimated after dividing the y -range into bins as defined in Sec. 3.4.1.1:

$$y_s = y_{min} + i_s \Delta Y \quad \text{with } i_s = 0 \dots N_y - 2 \quad (3.4)$$

With y_s the lower boundary of a Y -bin, and $y_s + \Delta Y$ the corresponding upper boundary. Standard tracking [39] is used to identify the displacements of those particles that remain in the same bin during a unit time step. Averaging over all particles and time steps then produces the mean local velocity in the x -direction:

$$v_x(y) = \sum_{i,k \in \{Y_s\}} \Delta x_i(t_k) / \sum_{i,k \in \{Y_s\}} \Delta t \quad (3.5)$$

where $i, k \in \{Y_s\}$ if $y_s < \{y_i(t_k), y_i(t_{k+1})\} < y_s + \Delta Y$

Here $\Delta x_i(t_k)$ is the displacement of particle i between t_k and t_{k+1} . To make the measurement of $v_x(y)$ slightly more accurate, the y -value assigned to $v_x(y)$ is set equal to the average y -position of the tracked particles (rather than the midpoint y -value of the bin).

Depending on the experiment and the iteration stage, the measured velocity profile may look noisy, due to the finite number of observations. In the first iteration, the Y -bins are usually chosen narrow. A relatively large fraction of the particles may then remain undetected because lateral diffusive steps take them into another Y -bin. Other reasons for poor statistics are a low particle concentration or a short duration of the experiment. Noise is removed by a judicious smoothening. Velocity

profiles are very often gradual, as required by the spatial continuity of the mechanical stress in the fluid.

3.4.1.3 Ending the iterations

Repeating operations as described in Secs. 3.4.1.1 and 3.4.1.2, results in progressively better estimates of the velocity profile and hence in more reliable tracking. The reason is that subtraction of the advective displacements before tracking, diminishes the probability of misidentifications. This was illustrated in Fig. 3.5 (right panel): locations of the same particle in subsequent frames will be closer, making it less likely that another particle happens to be even closer. The improved correction for affine motion also allows choosing a smaller Δr_{max} per iteration step.

Fig. 3.5: Cartoon of the second step of the tracking procedure. Particle configurations are compared before and after a unit time step Δt . The left and middle panels are similar to Fig. 3.4. The right panel shows that after correction for local advection, the residual displacements are much smaller. This allows use of a smaller search radius in the tracking step (compare the faded and non-faded dots). In this example the estimated $v_x(y)$ is already quite accurate.

Ultimately, the smallest value for Δr_{max} will be dictated by the need to capture all the diffusive displacements. As long as the latter are smaller than the typical interparticle distance in the fluid, tracking should be possible [33]. Since the chance of finding a ‘ghost particle’ within the search radius strongly diminishes, also the need for restricting the tracking to Y-bins vanishes. Therefore in a typical

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iteration path, Δr_{max} is gradually reduced, while the bin with ΔY is increased. The (evolutions of the) values of these parameters are manually set.

3.4.1.4 Constructing trajectories

Trajectories are obtained by linking together all steps that were taken by the same particle:

$$x_i(t_j) = x_i(t_{i0}) + \sum_{k=i0}^j \Delta x_i(t_k) \quad \text{with} \quad \Delta x_i(t_k) = x_i(t_{k+1}) - x_i(t_k) \quad (3.6)$$

and likewise for displacements in the y-direction. In this (standard) expression, t_{i0} is the real time at the beginning of the particular trajectory. Specific for our method is that, because of the pairwise tracking (Sec. 3.4.1.1), the starting point of the linking operation is a set of single-step trajectories that contains (inherent) redundancies. Many particle-time records (x_i, y_i, t_k) occur twice: as the end point of the step from t_{k-1} to t_k and as the starting point of the step from t_k to t_{k+1} . The trajectory labels l_t are different however. This problem is tackled by assigning an additional label l_k to each data record, so it will contain $(x_i, y_i, t_k, l_k, l_t)$. Multi-step trajectories are then created by a clustering operation that first groups all records that have either l_k or l_t in common, and subsequently eliminates the redundancies and assigns a new trajectory label. Optionally, this clustering operation can be aborted at a set maximum trajectory length; remaining locations of the involved particle are then analyzed as if they belong to a new particle. This option can be useful in the calculation of y-dependent MSDs (Secs. 3.4.3 and 3.5.3.2).

3.4.2 Removing advection

For statistical analysis of the stochastic displacements, the advection needs to be removed from the trajectories. This is achieved by subtracting from each $\Delta x_i(t_k)$, the measured average displacement in the x-direction, at the instantaneous y-location $y_i(t_k)$:

$$x'_i(t_j) = x_i(t_j) - \sum_{k=i0}^j v_x(y_i(t_k))\Delta t \quad (3.7a)$$

$$\Delta x'_i(t_k) = \Delta x_i(t_k) - v_x(y_i(t_k))\Delta t \quad (3.7b)$$

where $v_x(y_i)$ is interpolated from the measured velocity profile. This operation keeps the linkage of the trajectories intact, but the displacement steps should now

become purely stochastic. Note that displacements in the y -direction remain unaffected. The difference between the ‘real’ trajectories $r_i(t_k \dots t_j)$ and the ‘residual’ trajectories $r'_i(t_k \dots t_j)$ obtained using Eq. 3.7 is illustrated in Fig. 3.6.

Fig. 3.6: ‘Real’ and ‘residual’ trajectories. The latter are obtained from the former by subtraction of the instantaneous advective motion.

In case of a time-dependent flow, the following extension is made:

$$v_x(y, t) = v_x(y) \times f(t) \quad (3.8)$$

where

$$f(t_k) = \sum_{iy=1}^{N_y} \frac{v_x(y(iy), t_k)}{v_x(y(iy))} / N_y \quad \text{with} \quad y(iy) = y_{min} + (iy - 1)\Delta Y \quad (3.9)$$

Here the ΔY corresponds to a new binning of the Y -range (optimized for measuring fluctuations in flow rate). The idea behind this binning is to reduce the sensitivity of $f(t)$ to dis/appearances of particles from/in flow lanes with low or high speeds. In words, Eq. 3.8 means that the flow rate is considered time-dependent, but the shape of the velocity profile assumed to remain the same.

3.4.3 Calculating Mean Squared Displacements

Given the advection-free trajectories, calculation of the Mean Squared Displacements in the x - and y -directions is straightforward. In channel flow the MSDs may depend on the y -location, due to possible influences of walls and

3.5 Results and Discussion

velocity gradients [36]. Measurement of this dependence is done by calculating for each trajectory i the average y-location $\langle y \rangle_i$, and using the distribution of the found $\langle y \rangle$ values as a basis for making a new binning of the Y-range (now optimized for measuring MSDs). In equation form:

$$\langle y \rangle_i = \sum_{k=i0}^{k_{imax}} y_i(t_k) / \sum_{k=i0}^{k_{imax}} \quad (3.10)$$

where k_i labels the real time (or frame number): k_{i0} is the beginning of the particular trajectory while $k_{imax+1} - k_{i0} + 1$ is its length. The local x-MSD in a particular Y-bin is then given by:

$$MSD_{x'}(y, n\Delta t) = \sum_{i \in \{Y_s\}} \sum_{k=i0}^{k_{imax}-n} [x'_i(t_{k+n}) - x'_i(t_k)]^2 / \sum_{i \in \{Y_s\}} \sum_{k=i0}^{k_{imax}-n} \quad (3.11)$$

where $n\Delta t$ is lagtime, and the $\langle y \rangle$ -locations have to fall between the boundaries of the bin:

$$i_{\langle y \rangle} \in \{Y_s\} \quad \text{if } y_s < \langle y \rangle_i < y_s + \Delta Y \quad (3.12)$$

The y-position of the bins itself is taken at the midpoint between the boundaries. In the calculation of the y-MSD, x'_i has to be replaced by y'_i in Eq. 3.11.

While the calculation of the MSDs according to Eqs. 3.10-12 is fairly simple, and can be achieved with the standard routine [39], there are two specific points of attention. Firstly, the Y-binning (or Y-resolution of the MSD) has to be chosen judiciously: this is a matter of the number of displacement steps and possibly also the distribution of the latter over the entire y-range. Secondly, for long trajectories, $\langle y \rangle_i$ may no longer be completely representative for the Y-bin as assigned via Eq. 3.12: the particle might have visited neighboring Y-bins as well. Compromises in the y-resolution of the MSD arising from this effect can be mitigated by segmentation of trajectories into fragments with a preset maximum length (Sec. 3.4.1.4).

3.5 Results and Discussion

3.5.1 Computer simulations

Since the computer simulations provided possibilities to test our analysis method for a broader range of parameters, we discuss most of our results here. Roughly speaking, two performance levels can be identified; the first level being a correct measurement of the velocity profile via particle tracking, and the second (more

demanding) level comprising the measurement of the reliable MSDs via careful subtraction of the local advection.

All simulated datasets were analyzed with the same parameter settings. Four iterations were used to obtain the trajectories, reducing the number of Y-bins (flow lanes) sequentially as 100, 40, 10, 3 and the corresponding maximum displacements (search radii) as 8, 4, 4 and 4 pixels. Typically only results of the last iteration will be presented. Areas close to the boundaries of the final 3 Y-bins used during tracking, were excluded from the analysis, to avoid negative biasing of the found D_y values. In the construction of trajectories, the length was maximized to 12 steps; longer trajectories were cut into units of 12 steps, which were then treated as individual trajectories. This was supposed to contribute to a more even spreading of the mass-centers of the trajectories over the available y-range, and also to a better y-resolution of these quantities (Sec. 3.4.3). Mean Squared Displacements were fitted with a linear function using the first 7 lag times, after which the slope was taken as the measured diffusion coefficient, following the Einstein relation.

3.5.1.1 Velocity profiles

Measurement of the velocity profiles turned out to work successfully for all explored conditions, without the need for (nonzero) initial estimates for $v_x(y)$. An issue at low concentration ($AF=0.032$) was the occasional occurrence of empty Y-bins (for the entire time range) in the first iteration. This was addressed by deleting the data points for these bins; the ensuing problem of gapped $v_x(y)$ data in the next iteration was automatically handled by the software via interpolation between the available data points. Convergence of the velocity profile was always reached within 3 iterations; in most cases the first 2 measurements already superimposed well. Exceptions were only found in cases where v_{max} exceeded 6 pixel/frame.

Fig. 3.7 shows the stepwise improvement for a simulation at the highest flow rate. Although the first used Δr_{max} equals the largest advective displacement (8 pixels), the initially measured velocities are lower. This can be due to two effects: i) additional diffusive displacements cause Δr to exceed 8 pixels, leading to ‘filtering out’ of the largest displacements and hence negative biasing, or ii) another particle in the same Y-bin is trailing so closely that its displacement brings it closer to the

original position of the leading particle than the leader itself. In the latter case, which most likely occurs at the highest velocity, the ensuing misidentification

Fig. 3.7: velocity profile for $v_{\max}=8.0$ pixel/frame and $\sigma_x^2 = 0.36$ pixel²/frame at $AF=0.32$, measured in 3 iterations: 1) black squares, 2) red circles, 3) blue stars.

leads to a measured displacement in the negative flow direction; this explains the dimple in the initial $v_x(y)$. In subsequent iteration steps this error is rectified by biasing the search towards forward displacements. Additionally, the measurement accuracy also is improved stepwise via the larger total number of particles that are tracked as the Y-bins are made wider. For low particle concentrations, the finally obtained $v_x(y)$ is relatively less accurate, even though the number of data records was the same (10^6); this can be seen by comparing Fig. 3.7 and Fig. 3. 9.

3.5.1.2 Diffusion coefficients

The diffusion coefficients extracted from the simulated data were inspected using graphs of $\sigma_x^2 (= 2D_x)$ and $\sigma_y^2 (= 2D_y)$ as a function of y . Exploring broad ranges of diffusion coefficients ($\sigma_x(y)^2 = 0.04$ -1.0 pixel²/frame) and maximum flow velocities

(0-8 pixel/frame) at 3 discrete area fractions (0.032, 0.32, 0.43), we found that the inputted (equal and y -independent) D_x and D_y were fairly well recovered in the majority of cases.

3.5.1.2.1 General Trends

Typical results are illustrated in Fig. 3.8 for $AF = 0.32$, $v_{\max} = 8$ pixel/frame, and a variety of diffusion coefficients. In all cases statistical noise is encountered, as illustrated by the ‘spiky’ nature of the variation with y , and the lack of a perfect symmetry with respect to $y = 0$. Variation of the number of data records confirmed that the noise can be progressively reduced by increasing this number. A constant value of 10^6 was chosen for all simulations presented here. Besides this random noise, also systematic dependences of the relative errors in D_x and D_y on the magnitude of the diffusion coefficient and on the y -location appear present.

One systematic error observed for the largest diffusion coefficients, is that the measured D_x and D_y fall slightly below their input values. This effect, which is noticeable for $\sigma_{x(y)}^2 = 0.64$ and 1.0 pixel²/frame in Fig. 3.8, is due to the use of $\Delta r_{\max} = 4$ pixels in the last iteration. Even though this number is significantly above the standard deviation σ of the Gaussian diffusive displacements (0.8 and 1.0 pixels), the rejection of displacements $\Delta r > 2.83\sigma$ (respectively 3.16σ) still lowers the measured second moment (i.e. the MSD of a single step) by as much as 15% (7%). Mitigation of this issue by choosing a larger $\Delta r_{\max}$ would be possible for the lower area fraction of 0.032, but at high area fractions the correlation problem described in Section 3.4.1.1 then shows up.

A second systematic error is found for D_x , which shows a positive deviation at combinations of small D_x , large $|y|$ and high flow rates. This is observable in Fig. 3.8 (corresponding to the highest flow rate) for $\sigma_x^2 = 0.04$ and 0.09 pixel²/frame. Considering that in our case the shear rate is proportional to $|y|$, a plausible explanation might be the occurrence of unaccounted (small) diffusive displacements Δ_y into different flow lanes, causing an error $\Delta_y \dot{\gamma} \tau_0$ in the subtracted advection and hence an overestimation of the x -MSD:

$$\langle (\Delta x)^2 \rangle(\tau) = (\sigma_x^2 + (\sigma_y \dot{\gamma})^2 \tau_0) \times \tau \quad (3.13)$$

where $\tau_0 = 1$ frame since the v_x -value used in the advection correction was evaluated for each individual time step (see Eq. 3.7). For $\sigma_x = \sigma_y$ and $\dot{\gamma} = 0.16/\text{frame}$

(the highest shear rate), Eq. 3.13 predicts a 3% increase in apparent D_x , which is much lower than the one observed in Fig. 3.8. Moreover Eq. 3.13 also indicates that the relative error should be the same for all σ , which is not in line with the trend in Fig. 3.8.

Fig. 3.8: Measured σ_x^2 (red circles) and σ_y^2 (black diamonds) compared to input values (dashed lines) in a simulation where particles are advected via a parabolic profile (symmetric around $Y = 0$) with a maximum velocity of 8.0 pixel/frame, and additionally show diffusion with coefficients ($\sigma_x = \sigma_y = \sigma_z$) of 0.04, 0.09, 0.16, 0.36, 0.64 and 1.0 pixel. Area fraction is 0.32.

Alternatively, an inaccuracy Δv_x in the measured local velocity $v_x(y)$ would produce an x-MSD given by:

$$\langle(\Delta x)^2\rangle(\tau) = (\sigma_x^2 + (\Delta v_x)^2\tau)\tau \quad (3.14)$$

For relatively small Δv_x and τ , the quadratic term will not be conspicuous, but it can still contribute significantly to the apparent D_x as found by fitting the x-MSD with a linear dependence on the lag time. Clearly the error should become most noticeable at small σ_x . Taking the (worst) case of $\sigma_x^2 = 0.04$ pixel²/frame and $\Delta v_x = 0.06$ pixel/frame (a typical number from the simulation data), a 70% increase in apparent D_x is obtained from a linear fit to Eq. 3.14. This noise level is in reasonable agreement with Fig. 3.8. Also for the lower flowrates a fairly good agreement with Eq. 3.14 is found (not shown).

The remaining question, why the error increases with $|y|$ can be addressed by considering that near the walls, the flow velocities are lower. Particles flowing there have a longer residence time in the simulation box, and hence are not refreshed as often. Especially in combination with a low σ_y and σ_z (which tend to keep particles in the same y -bin and focal z -plane) this leads to a relatively poor sampling of the y -range and hence a less accurate measurement of the local $v_x(y)$. Recalculation of the x -MSDs, now using the (perfectly parabolic) input velocity profiles to eliminate the convection, produced a strong reduction of the y -dependent error in D_x . This finding, illustrated in Fig. 3.9, corroborates that indeed the direct error in Δv_x is responsible.

3.5.1.2.2 Specific Issues at Low and High Concentrations

While it is clear from the above that the measurement of accurate (x -) MSDs is generally more difficult at high flow velocities and low diffusion coefficients, it also appears that the regimes of low and high particle concentrations present their own specific issues.

At small area fractions, noise in the velocity profile (Eq. 3.14) is a prominent source of error. Even when taking the number of time steps inversely proportional to the number of particles per frame (to keep the product constant at 10^6), the obtained $v_x(y)$ data are more noisy at low AF. Here the y -bins become less evenly populated, giving less accurate measurements of v_x in the most underpopulated bins. The origin lies in the random insertion of new particles. At higher AF, these are less random because the area exclusion between particles leads to many rejections, thus favoring the more empty areas for insertions of new particles. The effect of a noisy $v_x(y)$ on the measured D_x is illustrated in Fig. 3.9.

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Fig. 3.9: Effect of errors in the measured flow velocity on the measurement of σ_x^2 at low concentration (AF: 0.032). Left: measured velocity profile for $v_{\max} = 8.0$ pixel/frame and $\sigma_x^2 = 0.04$ pixel²/frame. Right: apparent $D_x(y)$ based on the measured (red dots) and the ideal (black diamonds) $v_x(y)$, for $\sigma_x^2 = 0.04$ and 0.09 . The former data have been multiplied with 0.1 to improve the clarity of the plot.

At large area fractions (AF=0.43), the main source of error is misidentification, i.e. the occurrence of found trajectories that involve more than one particle. The fraction of thus flawed trajectories was determined by detecting for changes in particle identifier within a trajectory, and was found to increase non-linearly with

Fig. 3.10: Effect of tracking errors on measured diffusion coefficients at high concentration (AF=0.43). Maximum flow velocity is 8.0 pixel/frame, $\sigma_{x(y)}^2$ is 0.04 pixel²/frame. Red dots correspond to σ_x^2 , black squares to σ_y^2 . Closed symbols show the results of the analysis, while the open ones were calculated after removing the flawed trajectories.

particle concentration: for $AF = 0.032$ it is always < 10 ppm, making its contribution to the errors in the MSD negligible. However for $AF = 0.32$ it can increase up to 1.6% while for $AF = 0.43$ it can reach up to 7.6%. This is illustrated in Table 3.1 and Fig. 3.10.

The explanation for this dependence on particle concentration is straightforward: in more crowded systems, particles occur in closer proximity, making it more likely that more than one particle will occur within the search-circle defined by Δr_{max} . Combined with the random (x,y) displacements of these neighboring particles, this leads to increased chance of misidentification. The clear dependence of the error fraction on σ in Table 3.1 is also consistent with this picture: a larger diffusion coefficient will lead to more ‘scrambling’ (just as in a quiescent system). The dependence of the error on v_{max} is relatively weak, and shows a clear trend only for low diffusivities: if the random displacements are small, then cases leading to particle misidentification will mainly be generated via differences in advection; the probability of this effect increases with the shear rate and hence with the maximum velocity.

Table 3.1: Fraction of trajectories (expressed as %) that contain one or more link-up errors, as a function of v_{max} and σ , for area fractions of 0.32 (left) and 0.43 (right).

AF=0.32							AF=0.43						
	v_{max}	0	2	4	6	8		v_{max}	0	2	4	6	8
σ							σ						
0.2		0.02 2	0.042	0.06 8	0.08 5	0.12	0.2		0.41	0.61	0.78	0.96	1.1
0.3		0.07 0	0.099	0.13	0.17	0.20	0.3		1.1	1.3	1.4	1.6	1.8
0.4		0.16	0.20	0.23	0.26	0.30	0.4		1.9	2.0	2.2	2.4	2.5
0.6		0.48	0.50	0.53	0.58	0.61	0.6		3.7	3.9	4.0	4.1	4.2
0.8		0.93	0.95	1.0	1.03	1.1	0.8		5.7	5.7	5.8	5.9	6.0
1.0		1.5	1.5	1.5	1.6	1.6	1.0		7.5	7.5	7.6	7.6	6.0

Finally we present overall accuracies in the measured diffusion coefficients for all 90 flow experiments that were simulated. Since we did not aim for a spatially resolved overall analysis and because a ‘break down’ of the errors into specific mechanisms (as done above) is not always possible, we present results that are lumped over the entire y-range. Specifically, for the data sets shown in Fig. 3.8 and similar for all other flow rates, the difference between the locally measured D and the level of the dashed line was taken as the local error. From the local errors

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within the same data set, Root Mean Squares were calculated, and presented in Table 3.2.

The trends in this Table mostly confirm the expectations: relative errors are largest for small diffusivities and high velocities. Comparing Tables 3.1 and 3.2, it becomes clear that tracking errors are most influential for low diffusivities, even though the fraction of misidentified trajectories is larger for high diffusivities. This is attributed to the relative importance of the misidentified displacement: assuming that it will have a typical magnitude comparable to the interparticle distance, the anomaly of such a displacement will be stronger if the typical diffusive displacements are smaller. This issue, and its possible mitigations, have been described in [44].

While the precise numbers in the Tables will clearly vary with the chosen y-binning of D_x and D_y , and could show (weak) dependence on particular details of the simulations as well (e.g. the z-range of the simulation box), the trends of the errors are believed to be correct, and the typical magnitudes in the right range. As such they could be useful as a guideline in designing experiments. Since σ and $v_{\max}$ are expressed in pixels and frames, translation of these results to an optimized pixel binning and exposure time for a specific experimental situation should be relatively straightforward.

Table 3.2: Aggregated relative errors in diffusion coefficient along x (top) and y (bottom). AF is the area fraction occupied by the particles, σ is the standard deviation of the diffusive displacement and v is the flow velocity at the centerline of the channel.

AF=0.032

D_x	v	0	2	4	6	8
σ						
0.2		3.1	5.9	22	27	85
0.3		4.2	8.1	12	16	46
0.4		2.9	3.2	5.8	9.8	20
0.6		3.2	3.5	3.0	4.1	7.8
0.8		3.9	3.3	3.2	3.3	3.9
1.0		3.4	4.3	3.4	2.7	4.6

D_y	v	0	2	4	6	8
σ						
0.2		2.8	3.3	3.7	3.3	3.2
0.3		2.7	3.2	3.9	3.9	4.4
0.4		3.2	3.6	4.2	3.4	3.5
0.6		3.5	3.4	3.9	3.3	3.0
0.8		4.2	3.8	4.7	3.8	3.5
1.0		4.5	5.1	5.3	4.4	4.6

AF=0.32

Dx	v	0	2	4	6	8
σ						
0.2		4.1	5.2	9.6	18	25
0.3		3.8	3.0	5.7	8.3	12
0.4		3.6	2.9	3.8	4.7	6.9
0.6		4.9	4.4	4.7	4.2	4.9
0.8		6.5	5.3	4.8	5.6	4.9
1.0		6.1	6.1	5.8	4.8	5.0

Dy	v	0	2	4	6	8
σ						
0.2		3.8	4.2	5.5	6.2	8.7
0.3		2.8	4.5	4.4	4.6	5.1
0.4		3.9	3.3	3.3	2.8	4.4
0.6		4.6	5.2	4.2	5.2	4.5
0.8		5.0	6.3	4.4	5.5	4.3
1.0		5.9	6.0	7.4	6.8	6.1

AF=0.43

Dx	v	0	2	4	6	8
σ						
0.2		19	34	45	72	80
0.3		14	20	29	34	42
0.4		9.6	13	19	21	27
0.6		4.6	5.6	7.3	8.5	12
0.8		4.2	4.5	4.6	6.1	6.2
1.0		6.4	6.4	5.9	5.2	5.2

Dy	v	0	2	4	6	8
σ						
0.2		18	30	42	48	57
0.3		16	18	22	28	32
0.4		11	11	16	16	19
0.6		5.4	4.7	6.8	7.3	7.0
0.8		4.9	5.0	5.9	4.6	5.3
1.0		8.1	8.0	7.8	8.0	6.6

3.5.2 Experiments

To further validate our analysis, we also applied it to experiments in a microfluidic channel. In this case also other potential sources of error can play a role, e.g. the quality of the imaging, the precision of the localization, drift of the microscope table and fluctuations in the flow rate. We demonstrate for a typical case that most of these errors can be kept small, or corrected for.

3.5.2.1 Velocity Profiles

Measurement of the velocity profile was achieved within 3 iterations for all experiments. The highest velocity (at the centerline of the channel) amounted $\approx 8 \mu\text{m/s}$, corresponding to ≈ 4 pixels/frame. The same parameters were used throughout the analysis, varying the number of Y-bins sequentially as [100, 50, 25] and the corresponding search radius (in pixels) as [6, 4, 3]. Here 100 Y-bins corresponded to a bin width of $0.3 \mu\text{m}$, equivalent to 0.3 particle diameters or 2.2 pixels. In all cases, the first estimate of $v_x(y)$ was already close to the final one: see Fig. 3.11 for an example.

Fig. 3.11: First (black symbols) and second iteration (red line) of a velocity profile measured at low volume fraction. First measured velocities are slightly underestimated in the center of the channel. Inset: comparison of the second measured $v_x(y)$ with a calculation for a Newtonian fluid (dots).

As shown by the inset of Fig. 3.11, the last iteration of the measured velocity profile corresponds well to a theoretical calculation [45] for a Newtonian fluid that is pumped through a rectangular channel of the same dimensions. Since dilute suspensions of hard spheres also show Newtonian behavior [46], the close correspondence further validates our method for measuring $v_x(y)$.

3.5.2.2 Mean Squared Displacements

Fig. 3.12 shows some representative Mean Squared Displacements (along the x- and y-directions) as obtained from the ‘residual trajectories’, after segmentation into fragments with a maximum length of 15 steps (see Sec. 3.4.1.4). All data sets

correspond to the same experiment (the same fluid, pressure drop and z-coordinate), but different y-locations inside the channel (excluding points within 5 μm from the wall). A correction for minor ($\approx 1\%$) variations in flow rate (see Sec. 3.4.2) was performed before calculating the MSDs.

Several observations can be made. Firstly, the differences between the MSDs taken at different y-locations are generally rather small. Secondly, the majority of x- and y-MSDs turn out to be equal within statistical accuracy. Both findings indicate that the stochastic motion that remains after removal of the affine motion, is isotropic as for a quiescent fluid. Moreover, inspection of (the first 8 points of) each MSD reveals that they show good linearity, as expected for Brownian motion in a Newtonian liquid. This indicates that they can be considered as a measurement of the viscosity, for which we find $\approx 106 \text{ mPa}\cdot\text{s}$ using the Einstein relation.

Fig. 3.12: Mean Squared Displacements along X and Y directions for the experiment shown in Fig. 3.11.

The same residual trajectories were also analyzed for the probability displacement functions. The results obtained for the central flow lane ($y = 0$) are presented in Fig. 3.13, show that the distributions are Gaussian for both the x- and y-directions. Also these data coincide well with each other. This corroborates once more that the elimination of the advective motion was successful.

Returning to Fig. 3.12, we remark that extrapolation of the MSD data to zero lagtime always results in a (positive) non-zero ordinate. This deviation from the

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Einstein relation is attributed to limitations in the accuracy of the particle localization, as discussed in ref [41]. Note that the offsets are small: taking $2 \times 10^{-3} \mu\text{m}^2$ as a typical number, gives a square root of 44 nm, which seem reasonable as an error, considering the image quality that could be obtained (Fig. 3.2). In the calculations of diffusion coefficients from the MSD data (see below), this offset has been treated as a ‘noise floor’.

Fig. 3.13: displacement probability functions for the x (red) and y (green) directions, measured at $y = 0 \pm 1 \mu\text{m}$ for the same experiment as shown in Fig. 3.11.

3.5.2.3 Drift Correction

3.5.2.3.1 Table Drift

Correction for drifts can be important in experiments with a long duration. In our experiments, drift of the microscope table occurred with a typical velocity v_d of 0.01 pixel/frame, corresponding to $\approx 2 \text{ nm/s}$ (per direction). By default, drift in the flow direction ends up in the measured $v_x(y)$. Separate measurement and correction could be done using a ‘marker’, like a particle that is stuck to a side wall of the channel [47, 48]. However for the present work, even the effect on the x-MSD was negligibly small. For the same reason, table drift in the Y-direction had a negligible influence on the y-MSD. In principle, y-drift can also affect the y-resolution of $v_x(y)$ through convolution with a function of width $v_d T$, with T the duration of the experiment. For the longest experiment ($T = 100 \text{ s}$) in this study this gives a width of $\approx 0.2 \mu\text{m}$ which is again negligible. For more narrow channels and/or longer lasting experiments the correction might still be needed. In that case, the average

particle displacement in the y -direction has to be measured frame by frame, smoothened and integrated over time as in the usual drift correction [39]. The obtained function $\Delta y(t)$ should then be subtracted from the time-dependent y -coordinates, after which the tracking needs to be redone.

3.5.2.3.2 Transient Flow

Also transient flows can play a role, even if they are not evidently visible from the video images. Similar to the effect discussed in the context of Eq. 3.14, they cause an error in the subtraction of advection, which in case of high flowrates can cause appreciable errors in the x -MSD. In our experiments with straight channels (i.e. no constrictions or expansions) the transients involved only the amplitude of $v_x(y)$ and not its shape; this was concluded after comparing the velocity profiles of different time segments, and was attributed to transients in the pressure drop. We found that after mechanical disturbances, whether intended (e.g. a change of reservoir height) or not, at least 1 minute was needed to obtain a stable flow rate again.

Variations in flowrate can be detected relatively simply using the standard procedure that measures drift from the trajectories [39]. However correction for the effect necessitated a modification of the procedure, the reason being that in spatially varying (e.g. Poiseuille-like) flows, the center-of-mass velocity of the particle ensemble becomes more sensitive to sampling issues. We observed that (dis)appearance (via advection or diffusion) of a particle from a low- or high-speed flow lane can add significant noise to the center-of-mass velocity, in particular for dilute suspensions. The correction described by Eqs. 3.8 and 3.9 mitigates this effect by measuring and normalizing the time-dependent v_x in different Y -bins (with judiciously chosen width). Y -regions within 5 particle diameters from the channel sidewalls were excluded, because of the large relative error after normalization with a low velocity.

An illustration of the success of this approach is given in Fig. 3.14, which shows an experiment where the flow rate was found to increase by more than 20% after a mechanical disturbance. In this particular case, a channel with a width of $60\ \mu\text{m}$ and a structured wall (for $Y = 3\text{--}8\ \mu\text{m}$) was used. The iterative measurement of the (time averaged) velocity profile shown in Panel a indicates that $v_x(y)$ could still be

Fig. 3.14: A case of time-dependent flow. Panel a: Velocity profile. Red diamonds, green dots and black triangles correspond to iteration 1, 2 and 3 respectively. Panel b: Time dependence of the normalized velocity. High-frequency noise (black line) is smoothed out (red line) before use of the signal to correct the trajectories. Panel c: MSD in the flow direction, before (red) and after (blue) the correction. These data were measured at $Y = 24 \mu\text{m}$, where $\langle v_x \rangle = 5 \mu\text{m/s}$ (see panel a). Panel d: D_x before (red) and after (blue) correction, calculated from a linear fit to the first 8 points of the MSD. Green symbols indicate D_y . The volume fraction was 0.3 for this suspension.

measured as usual, in spite of the large amplitude variations $f(t)$ shown in Panel b. In Panels c and d, x-MSDs before and after the correction for varying flow rate are compared. In this (admittedly extreme) case, the drift correction reduces the MSD down to a factor 1/6.

3.5.2.4 Experiments at Low Volume Fraction

A particular case that has hardly been considered so far, is the superposition of diffusion and shear flow of colloids in the dilute regime. Studies where colloids are used as flow tracers are well-known [19, 49] but also the diffusive motion contains information: under certain conditions mechanical properties of the local micro-environment can be inferred from the MSDs of the particles [24-26]. The case of colloids in a purely viscous environment provides first exploration of this potential application, by (effectively) measuring the viscosity η as a function of shear rate (since $D = kT/6\pi\eta a$).

Data shown in Fig. 3.15 correspond to a dilute suspension ($\phi=0.03$) of 1 μm silica spheres in water/ glycerol, flowing through a 30 μm wide microchannel with the velocity profile shown in Fig. 3.11. In comparison to the simulations, this experimental case contains additional (potential) contributions to the MSDs: localization errors and several types of drift, as well as hydrodynamic interactions between the particles. Inaccuracy in the localization, shown as the offset in Fig. 3.12, was taken into account by fitting the slope of the MSD. Variation in the flowrate ($\approx 1\%$ increase over the experiment) was mitigated using Eqs. 3.8 and 3.9.

First of all, the data show the expected overall trends: D_x and D_y appear to be equal to each other and independent of the local shear rate (exceptions indicated by triangular symbols are attributed to a wall effect [36]). This suggests that the advection and drifts were adequately subtracted, and that shear-induced hydrodynamic interactions, which would show a y -dependence [36] do not play any role of importance. Taking into account the outcomes of the simulations, the remaining noise level in D_x and D_y (or alternatively in η) is then most probably due to inaccuracies in the measured $v_x(y)$. Considering that in the experiment, $\sigma \approx 0.2$ pixel and $v_{\text{max}} \approx 4$ pixel/frame, we estimated the expected typical error level by doing calculations similar to those done for Table 2, but now adapted for the fewer data records and Y -bins. Thus we found expected relative errors of $5 \pm 1\%$ for D_y and $35 \pm 10\%$ for D_x (where the $\pm$ sign takes into account the inaccuracy in σ) the noise levels in Fig. 3.15 are $\approx 15\%$, for both D_x and D_y , which is not in perfect agreement but of the correct order of magnitude.

3.5.3 Comparison to Other Tracking Methods

While the correction procedures and subsequent error analysis at the level of MSDs (Sections 3.4.2-3.5.2) have not been previously presented for colloids diffusing in a shear flow, the method to find the trajectories (Section 3.4.1) has elements in common with some of the procedures mentioned in ref [33]. A practical difference with the Correlated Image Tracking method is that our method only uses the images for particle localization, and subsequently tracks the particles using only their coordinates. In all cases addressed in this study, tracking was successfully achieved without the need for an initial estimate of the velocity profile: $v_x(y) = 0$ provided a good enough start. CIT could be used in a slightly

Fig. 3.15: Diffusion coefficients in the x- and y-directions, measured as a function of the y-location in the channel, for the experiment shown in Figs. 11-13. D_x is plotted in black while D_y is plotted in red.

broader scope of applications, for example at are very high velocities: if the affine displacement within a flow lane becomes comparable to half the typical distance between particles, irreparable misidentifications would occur in the first iteration of our method. In that case, a crude (non-zero) estimate for $v_x(y)$ is needed, as could be generated with CIT. Both in ref [33] and in our work, CIT provides a suitable start, followed by an optional refinement at the level of the particle coordinates to achieve sub-pixel accuracy.

3.6 Conclusions

We developed an analysis, which extends and complements existing methods for tracking the advective and diffusive motions of colloidal particles in shear flow. Analysis of computer simulations and experiments indicates that our method can produce reliable results even for strong flows reaching local Peclet numbers of 50. Mean Squared Displacements, obtained by removing the instantaneous advective displacements from the trajectories, are sensitive both to the accuracy of the measured velocity profile and to the occurrence of tracking errors. As such, they provide on one hand a very suitable tool to validate the tracking, while on the other hand they indicate which level of accuracy is required to obtain reliable advection-free MSDs.

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Chapter 4

4 Effects of shear and walls on the diffusion of colloids in microchannels

Colloidal suspensions flowing through microchannels were studied for the effects of both shear flow and the proximity of walls on the particles' self-diffusion. Use of hydrostatic pressure to pump micron-sized silica spheres dispersed in water/glycerol through poly (dimethylsiloxane) channels with a cross section of $30\text{ }\mu\text{m} \times 24\text{ }\mu\text{m}$, allowed variation of the local Peclet number (Pe) from 0.01 to 50. To obtain the diffusion coefficients, image- time series from a Confocal Scanning Laser Microscope were analyzed with a method that, after finding particle trajectories, subtracts the instantaneous advective displacements and subsequently measures the slopes of the Mean Squared Displacement in the flow (x) and shear (y) directions. For dilute suspensions, the thus obtained D_x and D_y are close to the free diffusion coefficient, at all shear rates. In concentrated suspensions, a clear increase with Peclet number (for $Pe > 10$) is found, that is stronger for D_x than for D_y . This effect of shear-induced collisions is counteracted by the contribution of walls, which cause a strong local reduction in D_x and D_y .

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4.1 Introduction

Understanding the diffusion of colloidal particles in micro channel flows is important for both fundamental and practical reasons. Shear flows can be strong enough to cause anisotropy in the diffusion coefficient, which in turn can lead to structural inhomogeneity or ordering [1-6]. Additionally, the confining walls which are required to set up the flow, have their own influence on the particle dynamics. Especially how the combination of the two effects works out is far from understood, as most research efforts into (anomalous) diffusion have been focused on either the shear flow [7-18] or the wall-confinement at rest [19-27].

Fundamental studies of shear-induced diffusion at low volume fraction (where particle interactions are generally weak) were done for both Brownian [28-30] and non-Brownian [10, 17, 18] suspensions. Studies on dense colloidal suspensions are scarcer. In two recent papers addressing this regime, string formation in simple shear flow was observed [1, 2] and explained from anisotropy in the diffusion coefficient. Possible implications hereof for directionally dependent colloidal interactions were mentioned. Earlier, also shear-induced migration in concentrated suspensions was observed [16, 31-34] and explained using anisotropic diffusion. Stokesian Dynamics simulations [35, 36] have significantly contributed to the understanding of diffusion in concentrated systems by taking into account both the structural and hydrodynamic effects.

The current scarceness of investigations into shear-induced diffusion of Brownian suspensions [1, 8, 28, 29] could partly be ascribed to difficulties in measuring diffusive behavior that is superimposed onto a flow. This applies in particular to flows at high Peclet number, where relatively small thermal motions are superimposed onto large advective displacements. But also the complexity of the phenomenon may have hampered studies. Phenomena like anisotropic diffusion and structure formation have shown a rich behavior even for simple (e.g. hard sphere) systems in well-defined (e.g. simple shear) flows [37, 38]. Surprisingly, ordering of particles has been observed only in oscillatory shear flow and the reserchers [3] could not find any evidence of structuring in steady shear field. To what extent these phenomena could also be influenced by gradients in shear rate, is unclear at present. In pressure-driven channel flows, the shear deformation patterns are different than in Couette or parallel plate flows; this might have consequences for the spatial distribution of the particles and/or ordering in the fluid. A recent study [39] on charged colloids in electro-osmotically induced flow showed that the average diffusivity (in the flow direction) increases with flow velocity in strongly

4.1 Introduction

interacting systems, but not in weakly interacting or dilute systems. The spatial distribution of the diffusivity might have played a role but was not accessible.

Confining walls are expected to play a role, especially in narrow microscopic geometries where they occur in close proximity to all particles. But the spatial extent of their influence is only well-known for a single particle near a single wall, in absence of flow. Only few studies have been focused on diffusion in concentrated systems near walls [20, 21, 23]. The interplay between the effects of shear and wall on the diffusion has hitherto never been addressed (as far as we know).

From an applied perspective, knowledge about the diffusive behavior in flow is important to understand and design the mixing of particles, the spreading of a liquid plug, or the formation of concentration gradients perpendicular to the flow direction. This applies in particular to microfluidics, where colloids are used for various purposes. Most current applications concern dilute systems using particles as tracers or scavengers [40, 41], but the flow of concentrated colloidal fluids through micro channels (e.g. in filtration, or after on-chip synthesis) is emerging. Other practical scenarios where the diffusive behavior of particles plays a role are drug delivery [42], the operation of semi-solid flow batteries [43], the handling of nuclear waste [44], and stagnant or slowly moving slurries of clay or sand particles in geological rock formations [45].

Based on the foregoing considerations, it is clear that still a lot of understanding needs to be gained about how the diffusive behaviour of Brownian particles is influenced by the magnitude of the shear rate, its spatial variation and the proximity of the wall. In this work, we consider the diffusion coefficient (in two directions) of nearly hard sphere colloids in a Poiseuille-like flow, generated by pressure drop over a microfluidic channel. Use of rectangular flow geometry allows considering local flow patterns that are effectively 2-dimensional; the effects of shear and wall can then be studied in a single plane. Due to the lateral variation of the flow velocity, different local shear rates are probed for a given overall flow rate. Repeating the experiment for different pressure drops then allows to achieve the same shear rate at different distances from the wall. This is helpful in separating the contributions of the shear flow (i.e. local Peclet number) and the wall on the diffusion coefficients. We measure the diffusive behaviors by applying particle tracking on data that are collected with a Confocal Scanning Laser Microscope. While this method requires great care to ensure that the advective

displacements are adequately removed before the diffusive ones are analyzed⁴⁶, it offers two key advantages: i) the measurements are directional, i.e. both flow and shear directions are examined, and ii) the measurements are spatially resolved, i.e. a distinction is made between the different flow lanes. This makes the method particularly well suited for the study of micron-sized spheres under (nearly) refractive index matched conditions.

As such, it is complementary to other methods: (Confocal) Differential Dynamic Microscopy (DDM) [51-54] is able to handle also smaller particles and less transparent fluids, but does not offer positional resolution, and requires prior knowledge of the intermediate scattering function (ISF) [52] based on the suspension concentration. Without suitable theoretical models for ISF, DDM becomes difficult to especially for concentrated suspensions. Alternatively, Particle Image Velocimetry (PIV) [55-56] is more suited for measuring local velocities but less so for diffusion and gets obscured for a statistically inhomogeneous tracer patterns [55] or tracer flows coupled with Brownian motion.

We study a low volume fraction ($\Phi = 0.03$) to approach the dilute limit, and an intermediate concentration ($\Phi = 0.30$) to represent a typical situation for transport and mixing of colloids that interact intensely, but not strong enough to cause ordering in the fluid. By comparing these two cases we will inspect the contribution of interparticle collisions to shear-induced diffusion. The scope of addressed Peclet numbers comprises the sub-range of 0.01-50 for both concentrations, and as such is very well suited to examine both the thermally and hydrodynamically dominated regimes.

4.2 Experiments

All experiments were performed at room temperature (22 ± 1 °C).

4.2.1 Fluid Preparation

Silica spheres with a 0.5 μm diameter core tagged with Fluorescein Isothiocyanate (FITC) and a 1.0 μm outer diameter (2a) were synthesized [47, 48] and suspended in water–glycerol (1:4 by weight) mixtures. With this solvent the refractive index of the particles is nearly matched (close enough for confocal microscopy) while the viscosity $\eta \sim 100 \pm 5$ Pa·s. The fluorescence of the particles was found not to degrade even after years of storage. Also the colloidal stability was preserved over this period, in spite of the (omnipresent but weak) van der Waals attractions. This

4.2 Experiments

implies that the particles carry some weak surface charge. Inspection of suspensions with optical microscopy did not show any evidence for long range ordering. This suggests that the repulsions are only significant at short-ranges (see *Appendix 4A1*), and hence the particles should show a ‘nearly’ hard sphere behavior.

Volume fractions of 0.03 and 0.3 were achieved by mixing weighed amounts. Measuring the mass density and the ‘dry weight’ fraction of a silica stock dispersion in pure water, and assuming no excess mixing volumes gave a mass density of 1.89 g/ml for the silica. Using the solvent mass density of 1.20 g/ml, we then calculated how much water-glycerol mixture was needed to redisperse the silica present in a metered amount of stock. Solvent transfer was then achieved by a 4 times repeated centrifugation and resuspension.

4.2.2 Microfluidics and Microscopy

We used 2 cm long PDMS microchannels with rectangular cross-sections (Fig. 4.1a). The channel design was fabricated in SU-8 by lithography, replicated in PDMS, and bonded onto a 170 μm thick glass coverslip. Teflon tubing (0.91 mm inner diameter) was used to connect the inlet and outlet of the channel to elevated reservoirs with the colloidal suspension and the solvent, respectively. To facilitate the filling of the channel, it was first flushed with pure solvent. Subsequently the hydrostatic pressure drop was reversed to let the suspension flow in. After the particles had reached the other end, the pressure difference was set to zero and 10 minutes were waited to allow homogenization in the Y and Z directions. The flow rate inside the channel was tuned by adjusting (with sub-mm accuracy) the height difference between the fluid columns. The lowest centreline velocity that could thus be reached was of O (0.01 $\mu\text{m/s}$). The highest explored velocity was 10 $\mu\text{m/s}$, which was still low enough to avoid formation of a concentration peak at the channel centre [31, 32]. After adjusting the pressure head (typically 10 values were explored per experiment) 1 minute was given to let the flow become steady again. Observations were made at a distance of ~ 1 cm (10^4 particle diameters) from the channel inlet to avoid the entry length effect [31], and at the symmetry plane 12 μm above the bottom to eliminate vertical shear components.

Fig. 4.1: a) Schematic of the experimental setup. Typical (X,Y,Z) channel dimensions are 2 cm, 30 μm and 24 μm . b) Confocal image taken at a height of 12 μm from the bottom of a suspension at volume fraction 0.3, flowing through the channel from left to right with a maximum velocity of 5.4 $\mu\text{m/s}$. Scale bar: 10 μm .

Images (Fig. 4.1b) were obtained with an UltraView LCI10 Confocal Scanning Laser Microscope (CSLM) in fluorescence mode, using a 488nm laser, and a 100X/NA1.3 oil objective giving a field of (X, Y) view of $88 \times 67 \mu\text{m}^2$ and an effective pixel size of $0.135 \times 0.135 \mu\text{m}^2$. Most data were collected at a rate of 10 fps using a Hamamatsu 12 bit CCD camera. Typically, 500 frames were grabbed at $\Phi = 0.3$ while it was 1500 frames at $\Phi = 0.03$. Additionally, a few movies of the low volume fraction sample were collected at the same magnification and frame rates up to 100 fps using a Visitech Infinity-3 system equipped with a Hamamatsu (flash 4.0) camera.

Accurate localization (along Z) of the X,Y plane where the flow velocities are maximal, is important for avoiding contributions of velocity gradients in the Z direction. After setting the pressure drop, this Z location was determined visually by moving the objective using the piezo positioner and judging the (changes in) flow speed. To allow *a posteriori* verification, time series were recorded at different Z-locations. Our data analysis (as explained in Sec. 4.2.3) corroborated that the velocity profile in the vertical direction had the expected shape, and that the optimal Z- location was always very close to the mid-plane of the channel.

4.2.3 Data analysis

To measure the velocity profile we extended publicly available particle tracking codes [49, 50], to allow accurate measurement of diffusive motions that are superimposed onto a flow⁴⁶. Briefly, the flow velocity $v_x(y)$ is first measured by dividing the Y-range into bins and averaging intra-bin displacements over (many) frames. Using an iterative scheme, subtraction of the (estimated) advective displacements is used to improve the quality of the tracking per iteration step. The diffusive motions are obtained from the trajectories of the final iteration, by first subtracting the instantaneous advective displacements (this eliminates the effect of Taylor dispersion [8, 57]), subsequently calculating the Mean Squared Displacements in the x- and y-directions, and finally by fitting these obtained (lag-time dependent) MSDs to a straight line in order to obtain $D_x(y)$ and $D_y(y)$. The measured diffusion coefficients are short-time self-diffusion as the involved time scale ($O(10)$) is much smaller than the long-time ($O(100)$) measurements.

From the velocity profile $v_x(y)$, the local shear rate is determined by taking the gradient: $\dot{\gamma}(y) = \frac{dv_x}{dy}$, and subsequently converted to the dimensionless Peclet number (Pe), defined as the ratio between the Brownian diffusion time ($\tau_B = a^2/D_0$) and the advective diffusion time ($\tau_C = \dot{\gamma}^{-1}$) [31, 32]:

$$Pe = \frac{\tau_B}{\tau_C} = \frac{a^2 \dot{\gamma}(y)}{D_0} \quad (4.1)$$

where a is particle radius and D_0 is its free diffusivity in the dilute limit.

4.3 Results and Discussion

4.3.1 Velocity profiles

The velocity profiles measured at different pressure drops are illustrated in Fig. 4.2a for $\Phi = 0.03$ and in Fig. 4.2b for $\Phi = 0.3$. They appear smooth for all concentrations and pressure drops. The highest local velocity is $10 \mu\text{m/s}$. Since this produces elongated images of the particle for exposure times of 100 ms, some additional experiments were performed with a high-speed confocal system (sec. 4.2.3). At the lowest flow rate, the maximum velocity is only $0.01 \mu\text{m/s}$. The

smoothness and near-parabolic shapes of the velocity profiles indicates that they were accurately measured.

This is further corroborated by analysing the mechanics of the flow problem. For Newtonian fluids, the amplitude of $v_x(y)$ should be proportional to ΔP , while its shape should remain constant. The former turns out to be the case within the measurement accuracy of the pressure drop. In Figs. 4.2c and d we inspect the flow-rate dependence of the shape of $v_x(y)$ by normalizing each curve via its maximum. The changes in shape turn out to be small. Due to the way of normalizing, the largest deviations are seen near the walls, where velocities are lowest. This is best visible for $\Phi = 0.03$ (Fig. 4.2c). However, at this volume fraction the suspension should behave as a Newtonian liquid at all shear rates. The deviations at low velocities might be due to (x-) drift of the microscope table, which gets incorporated in the measured $v_x(y)$ as an offset. Usually in vibration isolated systems, a microscope table will always show a slow motion with respect to the objective (noise). This motion gets incorporated in the found trajectories of the particle. In experiments without flow, a correction for this drift is possible by tracking the center of mass of all particles. In flow experiments, the motion contains both the flow velocity and the table drift velocity. These two are difficult to separate, but generally the drift is negligible: except at very low local velocities.

In Figs. 4.2c and d, also a comparison is made with theoretical profiles for a Newtonian liquid in the given channel geometry. Assuming no-slip boundary conditions at the walls, the velocities can be expressed as [58]:

$$v_x(y, z) = \frac{4 h^2 \Delta P}{\pi^3 \eta_0 L} \sum_{n, odd}^{\infty} \frac{1}{n^3} \left[1 - \frac{\cosh\left(n\pi \frac{y}{h}\right)}{\cosh\left(n\pi \frac{w}{2h}\right)} \right] \sin\left(n\pi \frac{z}{h}\right) \quad (4.2)$$

with x , y and z and ΔP as previously defined, h , w and L the channel height, width and length, and η_0 the viscosity. The agreement between experiments and theory appears to be good. Small deviations near the walls might be caused by the finite size of the particles in the experiments: in reality the particles also need to rotate, to

Fig. 4.2: Particle velocity profiles across the channel for different pressure drops. Panels a) and b) show the measurements from the videos. Panels c) and d) show the comparison of normalized velocity profiles (black points) with theory (red lines). Particle volume fractions are 0.03 for a) and c), and 0.3 for b) and d).

accommodate the velocity gradient. This effect could change the flow pattern somewhat, especially close to the walls. The Newtonian velocity profile also appears to describe the experiments at $\Phi = 0.3$ well. In principle, flow curves of colloidal hard spheres should show a transition from a low- to a high-shear plateau around $\text{Pe} \approx 1$. Measurement of the viscosity of a similar (near) hard sphere suspension (water-glycerol mixture with $0.96 \mu\text{m}$ silica spheres at $\Phi = 0.34$) by Cheng *et al.* [59] for different shear rates, clearly shows the Newtonian nature of the suspension between Pe numbers 3 and 110. Summarizing, the deviations from the theoretical velocity profiles for Newtonian fluids are modest, and do not suggest that there are issues regarding the correctness of the measured particle velocities [60-62].

4.3.2 Diffusion Coefficients

Fig. 4.3: Mean Squared Displacements (MSD) for a suspension at $\Phi=0.3$, for the experiment where $v_{\max}=5.4 \text{ } \mu\text{m/s}$. Different datasets in the same panel correspond to different locations: from bottom to top $y=4.5, 5.6, 7.5, 9.7$ and $10.5 \text{ } \mu\text{m}$ from the centre line. This order corresponds to an increasing local shear rate ($\dot{\gamma}$). Panel a): MSDs in flow direction (after correction for advection) and panel b): MSDs in the velocity gradient direction. Solid lines are linear fits to the experimental data.

Typical MSDs obtained for an experiment at $\Phi = 0.3$ are shown in Fig. 4.3 for both flow (Fig. 4.3a) and shear (Fig. 4.3b) directions. The linearity of the data is good, also for the flow direction where (large) advective displacements had to be subtracted first. Both MSDs are found to depend on y -location; this is ascribed to the y -dependence of the local shear rate. Extrapolation of the linear fits to zero lag-time reveals that both MSDs have an offset of $\approx 70 \text{ nm}^2$. This value is close to the typical noise floor of an MSD measurement [27], but still contributes significantly to the magnitudes of the MSDs. Therefore D_x and D_y are calculated from the slopes of the linear fits to the MSDs (using the Einstein relation).

4.3.2.1 Influence of shear

In dilute suspensions ($\Phi = 0.03$), both D_x and D_y are practically equal to each other, and almost independent of the overall flow rate and the y -location (data shown elsewhere [46]) Exceptions to this are only found in close proximity of the

4.3 Results and Discussion

walls due to the (anisotropic) hydrodynamic resistance close to the wall. As the particles are only weakly interacting with each other in dilute suspensions, their diffusive behavior should be similar to that of a solitary particle; at rest as well as in flow. In contrast, for concentrated systems ($\Phi = 0.3$), both D_x and D_y do show a dependence on both overall flow rate and y -location. Representative examples are shown in Fig. 4.4 for a low and a high flow rate.

Fig. 4.4: Experimental results for a concentrated suspension ($\Phi=0.3$) nearly at rest (a) and in a strong flow (b). Upper graph: (black square) diffusion coefficients in the flow (x) and (red circle) shear (y) directions as a function of the lateral (y) position in the channel. Lower graph: Local velocity and shear rate in the same channel. The walls are located at $y = \pm 15 \mu\text{m}$. Symbols represent experimental data while lines are to guide the eye.

Analysing $D_x(y)$ and $D_y(y)$ in conjunction with the local shear rate $\dot{\gamma}(y)$ reveals that both diffusion coefficients are influenced by two opposing effects; i) first of all, the diffusion is enhanced by the local shear. At the centreline $y = 0$ where $\dot{\gamma}$ is zero, D_x and D_y are equal while for $|y| > 0$ both D_x and D_y show an (initial) increase. These observations can be attributed to shear-induced collisions, which are well known to occur also for non-colloidal fluids at high concentrations [8, 15,

16]. This increase turns out to be stronger for D_x than for D_y . ii) as the side walls are approached, the diffusion coefficients reach a maximum followed by a steep decrease. Considering that the shear rate shows a continuous increase up to the point where the wall is reached, this illustrates that the diminishing effect that the wall has on D_x and D_y , ultimately becomes dominant.

Fig. 4.5: Diffusion coefficients in the flow (x) and shear (y) directions as a function of lateral (y) position, for a suspension at $\Phi=0.3$ studied at different flow rates. At $y=0$, fluid elements are advected without any shear (irrespective of flow rates) and all the measured D_x and D_y coincides. Maximum flow velocities ($v_{\max}$): black squares: 1.44 $\mu\text{m/s}$, red circles: 2.24 $\mu\text{m/s}$, violet up-triangles: 3.05 $\mu\text{m/s}$, blue down-triangles: 3.89 $\mu\text{m/s}$, green diamonds: 4.75 $\mu\text{m/s}$. Symbols represent experimental data while lines are to guide the eye.

More insight regarding shear-induced diffusion and the wall effect can be obtained by collecting the results obtained at different pressure drops in the same graph (see Fig. 4.5). Besides a confirmation of the general trend, this also allows comparing D_x and D_y at the same y-location but different flow rates. Clearly, both D_x and D_y increase systematically with the flow rate, for all y-locations except at the center where $\dot{\gamma}$ is zero regardless of the velocity. This corroborates that both diffusion coefficients are enhanced by shear (to an extent that depends on the shear rate, or as we will see, the Peclet number).

To separate the contributions of the shear flow and the wall, we utilize the fact that many different overall flow rates were explored. As can also be seen from Fig. 4.2a

4.3 Results and Discussion

and b , each curve covers a range of slopes (i.e. shear rates), and the overlap is such that the same $\dot{\gamma}$ can often be found in several different curves: further away from the wall as the flow rate gets higher. This allows making graphs of D_x and D_y vs y , under the constraint that the shear rate is the same. Our analysis, most significantly, revealed that (at least) for $|y| \leq 0.7|y|_{max}$ the data at different velocities superimpose well. This finding, which is in good agreement with the observation that peaks in $D_x(y)$ and $D_y(y)$ are generally found at $|y| \approx 0.8|y|_{max}$ (see Figs. 4.4 and 4.5), has two implications. Firstly, away from the walls, the diffusion coefficients appear to be determined by the local shear rate only. This makes it possible to construct master plots for D_x and D_y as a function of $\dot{\gamma}$. And secondly, using these master plots, it should be possible to quantify the wall effect in presence of shear.

Fig. 4.6: Short time self-diffusion coefficients in the flow (x) and velocity gradient (y) directions, as a function of Peclet number (Pe). a) At $\Phi = 0.03$, diffusion is isotropic and independent of Pe number. b) At $\Phi = 0.3$, the diffusion coefficient is isotropic up to $Pe \approx 5$, after which it increases with Pe . Beyond $Pe = 10$, diffusion becomes strongly anisotropic. Red points(circle) are for D_y and black points(square) are for D_x . Blue dashed lines indicate the diffusion coefficient at $Pe = 0$.

We first discuss the effect of local shear alone. In Fig. 4.6 we plot D_x and D_y as a function of Peclet number. To make the plot more general, diffusion coefficients are normalized with respect to their value in absence of shear. Interestingly, for the dilute system ($\Phi = 0.03$, Fig. 4.6a), D_x and D_y are found to be equal within their uncertainty ranges, for all Peclet numbers. Moreover, a clear dependence on Peclet number is absent. This confirms that under dilute conditions, the motion of a particle is simply a superposition of an unimpaired Brownian diffusion and a spatially dependent advection (in the limiting case, all particle interactions are

neglected). Qiu et al [8], and Orihara and Takikawa [9, 28] who used an oscillating flow to study shear-induced diffusion in a very dilute system, observed a constant diffusivity perpendicular to the flow direction as well.

Considering the diffusivity in the flow direction, Orihara et.al. [9, 28] found a strong enhancement by shear. This apparent contrast with our results can be ascribed to the contribution of advection: unlike the earlier studies [9, 28], we have eliminated the local affine motions (in order to highlight the effect of shear induced collisions). Hence both the earlier and our present findings show that the particle motions in flow can be understood from a superposition.

It is interesting to compare our results to earlier findings. Cheng et. al. [1], studied a similar fluid in a plate-plate geometry, and found shear enhancement of the diffusion in the velocity and vorticity directions. Remarkably, they used a power law with an exponent of 0.81 to describe the lag-time dependence of the x-MSD, whereas we found a linear behavior. Considering the effects of spatial confinement [27] on MSD, this difference might be due to the stronger confinement (3 to 10 particle diameters) in their system. In an early study using Stokesian Dynamics, Bossis and Brady [13] observed a reduction of short-time self-diffusion coefficients with increasing shear. This opposing trend might be related to the fact that they considered a monolayer of colloids. The enhancement of the y-diffusion coefficient as we found, appears in good agreement with the shear induced migration of particles from the wall to the channel centre found by other researchers for concentrated suspensions at high Peclet number [31, 32].

4.3.2.2 Combined influence of wall and shear

Given the master curves for D_x and D_y as a function of Pe , it is possible to make a quantification of the contribution of the wall ΔD_x and ΔD_y , for different shear rates. We remark that in presence of (strong) flow, the calculated effects are less accurate than the data presented in Fig. 4.5 and Fig. 4.6, because the diffusion coefficients become rather small close to the wall and because more data processing steps (see *Appendix 4A2*) were needed to arrive at the results. Nevertheless they should still be interesting since they indicate trends that have never been measured. From the master plots (fig. 4.6), we extrapolated diffusion coefficients at all shear rates including near the wall. Measuring the difference between extrapolated and observed data for all experiments, we quantified the wall influence on diffusivity.

4.3 Results and Discussion

To assess the accuracy, we first consider the experiment at low volume fraction (0.03). Here the particles can be reasonably approximated as isolated species while the effect of shear is negligible. This renders a comparison of the measured D_x and D_y with the theoretical expressions meaningful. Approximatively, the reduction in diffusivity relative to the free diffusion coefficient D_0 can be expressed as:

$$\beta_x^{-1} = \frac{D_x}{D_0} \cong 1 - \frac{9}{16} \left(\frac{a}{\Delta y} \right) + O \left(\frac{a}{\Delta y} \right)^3 \quad (4.3)$$

for diffusion parallel to the wall [63-65], and

$$\beta_y = \frac{D_y}{D_0} \cong \frac{6\Delta y^2 + 2a\Delta y}{6\Delta y^2 + 9a\Delta y + 2a^2} \quad (4.4)$$

in the perpendicular direction [66]. Here a is the particle radius while Δy is the distance between particle centre and wall (note that $\Delta y \geq 0.5$). Defining $\Delta D_x(\Delta y)$ as $[1 - \frac{D_0 - D_x(\Delta y)}{D_0}]$, and similarly for $\Delta D_y(\Delta y)$, allows comparison of the experimental data with Eqs. 4.3 and 4.4. The agreement between solid lines and black symbols in Fig. 4.7 a and c turns out to be fairly good; it is the noise in the experimental data which precludes a more accurate comparison.

In the presence of shear flow, we define ΔD_x as $D_x(\Delta y) - D_x(Pe)$, where the latter term is interpolated from the master curve (Fig. 4.6) after looking up the Peclet number at Δy . A detailed description of the procedure can be found in the Appendix 4A2. Fig. 4.7 shows $\Delta D_x(\Delta y)$ and $\Delta D_y(\Delta y)$ as function of normalized distance ($\Delta y/d$) at rest and in flow for $\Phi = 0.03$ (panels a and c) and $\Phi = 0.3$ (panels b and d). It is suggested by all graphs that, after correcting for the direct effect of shear flow, the remaining deviation in the diffusion coefficient is mainly due to the wall. In other words: indirect effects of the shear flow (e.g. via a change of the local structure) are weak as compared to the local wall effect. This could be expected for $\Phi = 0.03$, but also appears to be the case for $\Phi = 0.3$.

Two additional remarks can be made: i) for $\Phi = 0.3$, D_x is less suppressed by the wall as compared to $\Phi = 0.03$ (Figs. 4.7 a and b), and ii) the typical length scale

over which D_x and D_y are influenced by the wall appears to be smaller for the concentrated fluid. This 'increased hydrodynamic screening' is in line with earlier experimental and theoretical measurements [23,67].

Fig. 4.7: Change in normalized diffusion coefficients as a function of normalized distance ($\Delta y/d$) from the wall. d ($= 2a$) is the particle diameter. Symbols show the experimental data, solid and dotted lines are the analytical solutions (Eqs. 4.3 and 4.4) while dashed lines indicate the free diffusion coefficient. Left panels [a,c] show the data for $\Phi = 0.03$. Maximum flow speed ($v_{\max}$): black square: $0.16 \mu\text{m/s}$, red circle: $5.4 \mu\text{m/s}$, green down-triangles: $10.6 \mu\text{m/s}$. Right panels [b,d] show the data for $\Phi = 0.3$. Here the dotted lines are plotted just to visualize the difference with the experimental data for $\Phi = 0.03$. $v_{\max}$: black square: $0.13 \mu\text{m/s}$, red circle: $0.80 \mu\text{m/s}$, green down-triangles: $4.0 \mu\text{m/s}$.

4.4 Conclusion

We studied the shear induced diffusion of dilute and concentrated Brownian near-hard sphere suspensions flowing through micro channels. Direct measurements of such diffusion coefficients in flow are scarce, and our results complement the existing literature. Our measurements indicate that the local Peclet number provides an adequate characterization of the effect of flow on diffusion (except close to the walls). Diffusion coefficients in the flow and velocity-gradient directions show different dependences on Pe for dilute and concentrated systems. At low volume fraction, both coefficients are equal and practically independent of the shear rate, in line with the definition. At high volume fraction, isotropic Brownian diffusion dominates at low Peclet numbers ($Pe < 1$) while for $Pe \gg 1$ both diffusion coefficients grow, due to shear-induced particle collisions. For $Pe > 10$ the diffusion becomes strongly anisotropic. Close to the wall, a strong reduction in diffusivity is observed for all concentrations and shear rates, indicating that as the wall is approached, the effect of the wall dominates over the effect of shear. We did not obtain evidence for a strong coupling between the walls and shear effects.

4.5 Appendix

Appendix 4A1

We measured the pair potential of silica spheres (diameter= $1\mu\text{m}$) in water-glycerol mixtures by approximately measuring the 2-dimensional radial distribution function ($g(r)$) [68]. The potential falls steeply to (near) zero within ≈ 50 nm. This distance seems comparable to other near-HS systems.

Fig. 4.8: Pair potential normalized by kT (blue circles) of silica spheres ($d = 1\mu\text{m}$; diameter) in water-glycerol solvent. r is the distance between two particle centers. $\Phi = 0.03$.

Appendix 4A2

For a neutrally buoyant particle in Newtonian liquid, the effective diffusion (D^{eff}) is equivalent to the Brownian diffusion (D_B)

$$D^{\text{eff}} = D_B \quad (4A1.0)$$

$$\frac{D^{\text{eff}}}{D_B} = 1 \quad (4A1.1)$$

In presence of a flat wall, the effective diffusion coefficient reduces due to wall influence

$$D^{\text{eff}} = D_B + D_w \quad (D_w \text{ indicates the influence of wall only}) \quad (4A2.0)$$

$$\frac{D^{\text{eff}}}{D_B} = 1 + \frac{D_w}{D_B} \quad (4A2.1)$$

This is same as H. Brenner's prediction. Now we assume that the shear effect acts additively with wall effect and hence shear induced diffusivity ($D_{\text{sh}}^{\text{eff}}$) can be expressed as

$$D_{\text{sh}}^{\text{eff}} = D_B + D_w + D_{\text{sh}} \quad (D_{\text{sh}} \text{ indicates the shear effect only}) \quad (4A3.0)$$

$$\frac{D_{\text{sh}}^{\text{eff}}}{D_B} = 1 + \frac{D_w}{D_B} + \frac{D_{\text{sh}}}{D_B} \quad (4A3.1)$$

The master curve is constructed considering the data points free from strong wall effect. So the extrapolated diffusivity (D_m^{extra}) from the master curve contains only the shear term which can be formulated by the following way

$$D_m^{\text{extra}} = D_B + D_{\text{sh}} \quad (4A4.0)$$

$$\frac{D_m^{\text{extra}}}{D_B} = 1 + \frac{D_{\text{sh}}}{D_B} \quad (4A4.1)$$

Now, if we subtract the observed diffusivity in shear ($D_{\text{sh}}^{\text{eff}}$) from the extrapolated diffusivity, we will end up of having the wall effect only and the relation becomes

$$D_m^{\text{extra}} - D_{\text{sh}}^{\text{eff}} = (D_B + D_{\text{sh}}) - (D_B + D_w + D_{\text{sh}}) = -D_w \quad (4A5.0)$$

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$$\frac{D_m^{\text{extra}} - D_{\text{sh}}^{\text{eff}}}{D_B} = - \frac{D_w}{D_B} \quad (4A5.1)$$

If we compare this with Brenner's prediction (comparing eq. A5.1 with eq. A2.1), then the relation becomes

$$D_{\text{Brenner}} = \frac{D^{\text{eff}}}{D_B} = 1 + \frac{D_w}{D_B} = 1 - \frac{D_m^{\text{extra}} - D_{\text{sh}}^{\text{eff}}}{D_B} \quad (4A6.0)$$

General normalized form can be represented as

$$\Delta D_i = 1 - \frac{D_{m,i} - D_i}{D_{Pe=0}} \quad , \quad i = x, y \quad (4A7.0)$$

where $D_{m,i}$ is the extrapolated diffusivity from master curve. So, for dilute concentration, wall effect on diffusivity at rest as well as in flow can be compared with analytical solution [63-66].

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Chapter 5

5 Apparent slip of colloidal suspensions in microchannel flow

We investigated the dependence of the apparent slip length (β) on the particle concentration for suspensions of colloidal hard spheres flowing through microchannels with smooth walls. Hydrostatic pressure was used to pump monodisperse suspensions of 1 μm silica spheres in water-glycerol mixture through a poly (dimethylsiloxane) microchannel with rectangular cross section. Image-time series recorded with Confocal Scanning Laser Microscopy allowed accurate measurement of particle velocity profiles via particle tracking velocimetry. Apparent slip lengths were measured by extra-polating the velocity profiles to zero. The two key variables in our work were the particle volume fraction Φ (0.03 - 0.42) and the Peclet number (2 - 50). Our study shows that the apparent slip length has a weak dependence on Pe , where the slip velocity near the wall grows linearly with shear rate irrespective of Φ . In contrast, β turns out to increase strongly with Φ , tending towards an asymptotic behavior for $\Phi \gg 0.3$. To explain these observations, we worked out a conceptually simple model, in which the apparent slip is caused by a local reduction in volume fraction due to excluded volume, and the local viscosity is calculated using the Krieger-Dougherty equation. The predictions by this model match the experimental results remarkably well.

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5.1 Introduction

Colloidal and non-colloidal suspensions are used in variety of applications, such as pharmaceuticals, food products, paints, cosmetics, ceramics, etc. For many of these products, knowledge of the slip behavior is essential for safe and optimum processing. Also applications where particle suspensions have to flow through meso/microscopic pores, like filters or microfluidic channels, can be affected by slip. Slip essentially reduces the drag coefficient for fluids flowing through a confined geometry, thereby enhancing the flow rate. In rheometry, i.e. the measurement of rheological properties such as the shear viscosity, the occurrence of slip ‘clouds’ the measurement, necessitating either mitigation or correction [1]. The presence of a smooth wall and the absence of strong particle-wall adhesion are generally considered as factors that favor slip.

Slip has been identified not only with particulate suspensions but also with molecular liquids, and several attempts have been made to quantify the slip in those systems using different measurement techniques [2-14]. In general it is found that for Newtonian liquids, the slip length depends on the interaction of liquid molecules with the substrate: wetting surfaces favour a no-slip condition whereas partially wetting or non-wetting surfaces cause noticeable slip. But the slip in molecular liquids, which can occur as a result of repulsive interactions of liquid molecules with the substrate, differs fundamentally from the ‘apparent’ slip found in suspensions. For particulate fluids, slip occurs due to the formation of a low viscous lubrication layer. Since the proximity of hard particles to a hard wall is hydrodynamically disfavored, flowing suspensions can be expected to expel a film of solvent, with a film thickness comparable to the particle size. The corresponding lowering of the particle concentration can cause a (strong) reduction in the local viscosity, and hence a large velocity gradient across this thin layer. Linear extrapolation of the velocity profile of the homogeneous suspension to the location of the wall then results in a finite velocity, which is often termed as the “apparent slip velocity”[15]. We remark that this definition of “apparent slip” differs from the concept of “true slip” as can occur in polymeric melts (with no solvent available for lubrication), or “friction slip” [16] which involves a Coulomb-friction mechanism.

While the formation of a thin molecular film can occur irrespective of the particle concentration, the importance of slip, i.e. the magnitude of the apparent slip length can clearly be expected to depend on the particle volume fraction. In a (very) dilute system, the relative viscosity η_r of the bulk suspension will not be very different from unity; the effect of particle depletion near the wall will then be relatively

5.1 Introduction

small. For higher bulk concentrations corresponding to $\eta_r \gg 1$ the effect should be much stronger. Also additional mechanisms leading to particle depletion near the walls could play a role, like shear-induced structural changes in the fluid.

Most studies aimed at slip in (concentrated) suspensions were performed with large, non-Brownian particles [14, 15, 17-21] showing a liquid-like or solid-like collective behavior. In their studies on concentrated suspensions of irregularly shaped particles, Yilmazer and Kalyon [17] found that the (normalized) apparent slip length scaled with the suspension viscosity: $\eta/8 \leq \beta/a \leq \eta/4$, where η is the relative viscosity and a is particle radius. Later Jana, *et.al.*[15] also reported a similar scaling for large hard sphere systems ($2a = 90\mu\text{m}$) at $\Phi \geq 0.45$, which they modelled with a shear-induced migration of the particles[22, 23] in Couette flow. However they did not observe significant slip for $\Phi \leq 0.40$.

Considering the large amount of work on non-Brownian particles, it is remarkable how little emphasis has been given to colloidal suspensions (even for the model case of hard spheres). Using rheo-microscopy Ballesta *et. al.* [8, 24] observed predominant slip behavior for concentrated ($\Phi \sim 0.58$) colloidal dispersions, and quantified a yielding transition from this. They also found a qualitative similarity of the slip behavior of concentrated suspensions of soft particles [25, 26] below the yield stress, and a Bingham-type slip response. Another study with Brownian suspensions ($\Phi = 0.28$) with different particle sizes $O(100\text{nm})$ by Hartman Kok *et. al.*[10] reported measurable wall-depletion effects at shear rates corresponding to a Peclet number of $O(1)$. At lower Pe , where the timescale of the Brownian motion is shorter than that of the flow, the fluid can restore the equilibrium structure in spite of the flow. However, a systematic study of the (apparent) slip length as a function of both Φ and Peclet number has been missing so far; most studies were done on the slip response near glass transition.

In the present study, we determine the apparent slip length of monodisperse suspensions of $1\mu\text{m}$ silica particles suspended in water-glycerol mixture using confocal microscope which allows to measure particle velocity near the wall by direct observation of particle displacement along the flow direction. The key variables are the volume fraction (varied from 0.03 to 0.42), and the Peclet number (varied from 2 to 50). The measurements will be compared to predictions from a model that accounts for the particle depletion near the wall using a simple geometric argument.

5.2 Theoretical modelling

Experimentally we measure the slip length β based on the Navier boundary condition which relates the slip velocity (v_w) at solid-liquid interface to the shear rate ($\dot{\gamma} = \frac{\partial v_x}{\partial y}$) tangentially applied on the surface:

$$v_w = \beta \frac{\partial v_x}{\partial y} \Big|_{y=y_w} \quad (5.1)$$

Accordingly, β is the distance to the wall at which the fluid velocity extrapolates to zero (fig.5.1). Slip becomes an important phenomenon if the magnitude of β becomes comparable to the length scale (e.g. width) of the flow geometry.

Fig. 5.1: (a) Schematic representation of wall slip based on Navier's boundary condition. $v_x(y)$ represents the local velocity profile near the wall, while v_w is the extrapolated velocity at the wall. β is the slip length. (b) Schematic of the calculation of the apparent slip length. The flow direction is parallel to the wall. The solid line is the effective velocity profile $v_x(y)$ whereas the dashed line indicates the extrapolated velocity to zero.

Our experimental observations are compared with a simplistic model considering just an excluded volume interaction between a spherical particle and a flat wall. The model ignores spatial correlations between particles, and hence assumes that the volume fraction is equal to the bulk concentration (Φ_∞) for all y coordinates, except in a transition zone $0 < y < 2a$ near the wall. In this zone, a local volume fraction is defined as the fraction of solid in a thin slice perpendicular to the y -direction, with $dy \ll a$. For the case of hard spheres with radius a , this concentration profile $\Phi(y)$ is expressed as (see *Appendix 5A*):

$$\Phi(y) = \Phi_\infty f(y) = \Phi_\infty \left(\frac{y}{2a} \right)^2 \left(3 - 2 \left(\frac{y}{2a} \right) \right) \quad (5.2)$$

To calculate the local viscosity $\eta(y)$ in the transition zone (the ‘lubrication layer’) from $\Phi(y)$, we insert the latter into the empirical equation by Krieger and Dougherty [27], which gives a good description of the viscosity of hard sphere suspensions:

$$\eta(\Phi(y)) = \eta_0 \left[1 - \frac{\Phi(y)}{\Phi_m} \right]^{-\frac{5}{2} \Phi_m} \quad (5.3)$$

where η_0 is the solvent viscosity and Φ_m is the maximum packing fraction of particles. The factor 5/2 in the exponent ensures that Einstein’s expression is recovered in the limit of low volume fraction [Einstein, 1956].

Theoretical velocity profiles $v_x(y)$ can now be calculated by combining Eqs. 5.2 and 5.3 with standard theory from fluid mechanics. Considering $v_x(y)$ as shown in fig. 5.1(b), the velocity at the end of the depleted layer at $y = 2a$ amounts v_c . The application of a constant shear stress (τ) applied to the different y -slices with varying $\Phi(y)$ creates a strong velocity gradient in the depleted layer. However, the slope of the effective velocity profile and the extrapolated profile towards the wall will be equal at $y = 2a$. Equating the slopes at $y = 2a$ produces:

$$\frac{v_c}{\beta + 2a} = \frac{\tau}{\eta(\Phi(y))} \quad (5.4)$$

which gives:

$$\beta = \frac{\eta(\Phi(y))}{\tau} v_c - 2a \quad (5.5)$$

Now, according to Newton’s law of viscosity, shear stress is also related to the shear rate:

$$\tau = \eta(\Phi(y)) \frac{dv_x(y)}{dy} \quad (5.6)$$

The velocity profile near the wall is then obtained from Eq. 5.6 by inserting Eq. 5.3:

$$\frac{dv_x(y)}{dy} = \frac{\tau}{\eta(\Phi(y))} = \frac{\tau}{\eta_0} \left[1 - \frac{\Phi(y)}{\Phi_m} \right]^{\frac{5}{2} \Phi_m} \quad (5.7)$$

Integrating eq. 5.7 over the entire width of the depletion layer (2a), we get the expression for v_c :

$$v_c = \int_0^{2a} \frac{\tau}{\eta_0} \left[1 - \frac{\Phi(y)}{\Phi_m} \right]^{\frac{5}{2}\Phi_m} dy \quad (5.8)$$

Replacing v_c in eq. 5.5, we finally obtain the general expression for the apparent slip length (β),

$$\beta = \left(1 - \frac{\Phi_\infty}{\Phi_m} \right)^{-\frac{5}{2}\Phi_m} \int_0^{2a} \left[1 - \frac{\Phi(y)}{\Phi_m} \right]^{\frac{5}{2}\Phi_m} dy - 2a \quad (5.9)$$

The prediction from this model is that β increases with particle volume fraction. This model (Eq. 5.9) has only one adjustable parameter Φ_m . The value of Φ_m for colloidal hard spheres in flow depends on the Peclet number, and it is found that $\Phi_m = 0.63 \pm 0.02$ for low shear limit whereas $\Phi_m = 0.70 \pm 0.02$ for high shear limit [28, 29]. In our analysis we consider $\Phi_m = 0.63$. Comparing β as measured by Eq. 5.1 and as derived from Eq. 5.9, we obtain the quantitative dependence of β on Φ .

5.3 Experimental Methods

5.3.1 Material preparation

Silica spheres of $1\mu\text{m}$ in diameter (2a) were synthesized [30] and suspended in water-glycerol (1:4 by weight) mixtures. Each particle was tagged with Fluorescein Isothiocyanate (FITC) in a core of diameter of 500nm . Using such core-shell particles makes it easier to distinguish individual particles in flow, even in concentrated suspensions. The chosen water-glycerol mixture provides an (almost perfect) refractive index matching with the silica spheres ($n_p = 1.46$). This has two advantages: i) the scattering of light is minimized, enabling observations deep inside the channel (more than $10\mu\text{m}$ from the bottom) without difficulties in the subsequent measurement of particle locations from the microscopy images, and ii) the Van der Waals attractions are minimized. To screen the surface charge of the silica spheres, 0.8mM LiCl salt was dissolved in the water-glycerol; the corresponding Debye length [32] is $\approx 7\text{ nm}$. Given the very weak attraction and the short ranged electrostatic repulsion, the suspension should behave as a (nearly) hard sphere system. We did not observe any aggregation of particles, even after several months of storage. Nine suspensions ($\Phi = 0.03$ to 0.42) were prepared by

5.3 Experimental Methods

diluting a stock solution of $\Phi = 0.42$, and stored in an air-tight containers to prevent changes in the solvent (water) content.

Fig. 5.2: (a) schematic of the experimental set-up (not drawn to scale). Blue and red dashed lines with arrows indicate the incident (laser) and reflected (fluorescent) light respectively. b) Typical confocal (x,y) image taken at $z = 12 \mu\text{m}$ in a suspension at $\Phi = 0.24$. Flow is along the x-direction. Scale bar: 10 μm .

5.3.2 Flow experiments and confocal microscopy

Our experimental set-up is shown in Fig. 5.2. We prepared the microchannels by standard soft lithography. SU8 molds of the channels were fabricated on a silicon wafer, after which the design was replicated in poly (dimethylsiloxane) (PDMS). Channels with a length of 2cm (along the x direction), a width of 30 μm (along y) and a height of 24 μm (along z) were bonded onto a 170 μm thick glass coverslip [33, 34]. A few experiments were performed with channels having a width of 25 μm . Before bonding, the coverslip was rinsed with methanol, acetone and isopropanol and treated with oxygen plasma along with the PDMS channel for 60s. The entry and exit of the channel were connected to elevated reservoirs of suspension and solvent respectively, using Teflon tubing with 0.91 mm inner

diameter. Particle-laden fluids were pumped through the microchannel by setting the height difference between the inlet and outlet reservoirs. After the suspension had reached the other end, we waited for few minutes (typically 7-8 min) to homogenize the suspension across channel cross-section. The flow rate inside the channel was properly controlled by changing the height difference between the liquid columns which allowed us to obtain a range of shear rates near the wall $O(0.0-2.0 \text{ s}^{-1})$. We performed all the experiments at low shear limit where shear induced particle migration is weak [35].

Observations of the suspension inside the microchannels were made with a (Hamamatsu) 12 bit CCD camera connected to an (Perkin Elmer) UltraView LCI10 Confocal Laser Scanning Microscope (CSLM) in fluorescence mode using a 488 nm solid state laser operated at 15 mW. To localize the individual particles with high precision ($\sim 20 \text{ nm}$ accuracy in the x,y plane), we used a 100X oil immersion objective with 1.3 numerical aperture which provides a $88 \times 67 \mu\text{m}^2$ field of view and an effective pixel size of $0.135 \times 0.135 \mu\text{m}^2$. The objective was mounted on a piezo transducer to move the focal plane vertically (perpendicular to the flow direction) and placed at a distance of $\sim 1 \text{ cm}$ (10^4 particle diameters) from the channel inlet to avoid the entry length effect [36]. After localizing the particle layer at the bottom of the channel, the objective was slowly moved to bring the channel centre ($z = 12 \mu\text{m}$) into focus. The flow rate was systematically varied by controlling the height of the suspension reservoir. Typically for each flow rate, 1500 images were recorded at a unit exposure time of 100 ms.

5.3.3 Particle localization and data analysis

Localization of individual particles per video frame was done based on the well-established method by Crocker and Grier [37], using publicly available codes written in interactive data language (IDL) [38]. The resulting data files containing only the particle coordinates and time stamps were then used to measure the velocity profiles iteratively by the technique described in ref. [39]. The flow profile $v_x(y)$ was measured by dividing the y-range into narrow bins (ultimate width $\approx 0.4 \mu\text{m}$), and by averaging over the intra-bin displacements along the x-direction for all frames. The thus obtained velocity profiles were extrapolated to zero by finding the best linear fit, using a y-range of $2-3 \mu\text{m}$ from the wall. The slip length (β) was then quantified from the y-location where the extrapolated $v_x(y)$ becomes zero, as also shown in Fig. 5.1. Shear rate is calculated from the slope of linear fits. The

5.4 Results and discussion

difference between the results on the left and right walls for all the flow measurements was used to estimate error bars.

Accurate localization of the boundary wall is important in the measurement of β . Given that the particles cannot penetrate the wall, the closest position of a particle centre must be one radius (a) away from the wall. Hence ‘true’ wall locations at small and large y were assigned by respectively subtracting and adding $0.5 \mu\text{m}$ to the locations as detected from the particle coordinates. Here ‘detection’ comprised measurement of the y -localizations where concentration profile showed cut-offs. These concentration profiles were generated by making histograms of the y -coordinates of all particles in all frames, after a correction for the microscope table drift. Considering that the polydispersity of the particles was about 5%, the localization error should be roughly the same, i.e. $\approx 50 \text{ nm}$. From the measured particle velocity profile $v_x(y)$, the shear rate ($\dot{\gamma}$) at the wall was determined by taking the gradient: $\dot{\gamma}(y) = \frac{dv_x}{dy}$ at $y = y_w$.

In order to obtain an analysis in normalized coordinates, and to examine the possible role of Brownian motion, we expressed the local shear as a local Peclet number, defined by [33, 35, 36],

$$Pe = \frac{6\pi\eta_0 a^3 \dot{\gamma}}{kT} \quad (5.10)$$

where a is the particle size, η_0 is solvent viscosity, k is the Boltzmann constant and T is temperature.

5.4 Results and discussion

5.4.1 Velocity profiles

Typical (particle) velocity profiles as measured from the CSLM images at different pressure drops (ΔP) are illustrated in Fig. 5.3 (a) for $\Phi = 0.09$ and in Fig 5.3(b) for $\Phi = 0.42$. All profiles are smooth and show a gradual increase with ΔP . The shape of $v_x(y)$ remains Poiseuille-like (as in Fig. 5.3a) at low particle volume fractions; this is in agreement with the Newtonian nature of the suspension and the almost-square geometry of the channel cross section [34]. Increasing the particle concentration leads to gradual changes in the shape of $v_x(y)$. At the highest volume fraction ($\Phi = 0.42$) the velocity profile has become flattened at the centre, indicating that the viscosities are higher there. This is often associated with shear thinning, but it could also be (partly) due to a slightly increased local

concentration: if both the volume fraction and the Peclet number are high, then shear induced diffusion could induce a net flux of particles towards the centre. Concentration peaks in such scenarios have been observed by other researchers [35, 36]. Attempts to corroborate this for our case by comparing the number of detected particles per y-bin, stranded because it was not possible to obtain the same counting efficiency in the different flow lanes.

Fig. 5.3: (color online) velocity profile across the channel. Different color relates to the different pressure drop applied to change the flow rate inside microchannel. (a) $\Phi = 0.09$ (b) 0.42 .

Zooming in on the velocity profiles near the walls, it already becomes apparent that the slip velocity also increases with ΔP ; this is not unexpected, since v_w is defined as the product of the slip length and the velocity gradient at the wall (see Eq. 5.1). If the latter grows roughly proportionally with the flow rate, then the slip length would have to show an even stronger relative decrease, to make the slip velocity get lower.

Another remark is, that the velocity profile of the suspension is based on the motion of the particles (along the flow direction). Since the particles are much larger than the solvent molecules, strictly speaking the flow pattern created around them should be taken into account. For example, for single tracers co-flowing with a Newtonian solvent, it is known that the actual particle speed falls behind that of the solvent, reaching only 94% of the latter [33]. The suspension velocity is then a

certain (weighted) average of those two. Still, from the particle speed we can quantify the apparent slip length by extrapolating the velocity to zero.

5.4.2 Slip velocity and apparent slip length vs wall shear rate

Now, we relate the slip velocity with the shear rate ($\dot{\gamma}_w$) at the wall which acts tangentially to the surface, shown in fig. 5.4a. Visual inspection of our movies revealed that in flow, no particles were sticking to any of the sidewalls. In agreement with this, the image analysis of the flowing suspensions produced non-zero velocities for the particles in closest proximity to the wall. These velocities, shown in Fig. 5.4a, are close to (but slightly lower than) the slip velocity (v_w) as defined in Fig. 5.1.

Fig. 5.4: (a) Velocity of particles at the wall, as a function of the local shear rate. Symbols represent experimental data while lines are linear fits. (b) Dependence of the apparent slip length on the normalized shear rate. Symbols are experimental data and the dashed lines are the respective theoretical values of β determined from the model, Eq. 5.9. Particle volume fractions (Φ): 0.03 (black squares), 0.18 (red circles), 0.35 (green upper triangles), 0.42 (blue lower triangles). Error bars are estimated from a comparison between the two opposing channel walls.

We observe a fairly linear increase of this ‘slip’ velocity with shear rate, similar to earlier observations with Non-Brownian particles [15, 17, 20]. Interestingly, the ‘slip’ velocity depends significantly on the particle concentration: a higher Φ produces to a higher slip velocity (at the same shear rate). Using the slope of the v_w - $\dot{\gamma}_w$ plot and the particle radius, one can also estimate β . The apparent slip lengths in Fig. 5.4b were calculated more precisely, by performing a linear least

squares fit to the velocity profile in the range of 2-3 particle diameters from the wall. Taking the ratio of the offset and slope of the fitted line then produces β directly as shown in Fig. 5.1b. These steps were performed on both sides of the velocity profiles, to get an idea about the accuracy.

In fig. 5.4b, β is plotted as a function of Pe for different Φ . Anticipating that the apparent slip length is directly related to the finite particle size, β has been normalized by the particle radius, a [15]. In contrast to existing work on non-Brownian suspensions, we found a slight decrease of β with shear rate for a certain Φ . It is interesting to note that a transition of the viscosity from the low shear to the high shear limit, would cause the maximum volume fraction Φ_m in Eq. 5.2 to increase, and accordingly the slip length to decrease (as also indicated in Fig. 5.5). Ignoring this possible trend, and taking the average magnitude of the apparent slip length, a clear increase of β with increasing particle volume fraction (Φ) is observed.

5.4.3 Slip length vs particle volume fraction

Finally, our experimental measurements of the apparent slip length for different particle volume fractions are presented and compared with the theoretical model (Eq. 5.9) in Fig. 5.5. Each data point represents an average over measurements at

Fig. 5.5: Change in apparent slip length with particle volume fraction. Symbols are the experimental data. Solid line (red) is the theoretical profile calculated from the model (Eq. 5.9) for $\Phi_m = 0.63$. Green and black dashed line show predictions for $\Phi_m = 0.70$ and 0.58 respectively.

different flow rates. Not only does the (magnitude of the) increase of β with Φ become clearly visible; it also appears that the model calculation matches the experimental data rather well. Only at low Φ (≤ 0.1) the theoretical result appears

5.5 Conclusions

to under-estimate the experimental β ; however this discrepancy may not be very significant considering the error in the experimental data. The good overall agreement is perhaps surprising, considering the crudeness of the model. It might imply that there is no inherent slip effect, and that instead of it, the concept of excluded volume alone might explain the apparent slip. Our result seems qualitatively similar to the previous study of slip length with non-Brownian suspensions[15] where β scales with the relative viscosity ($\eta/8$). We observed slightly larger (normalized) slip lengths for Brownian suspensions compared to the reports on non-Brownian particles.

5.5 Conclusions

The apparent slip length of near hard-sphere colloidal suspensions flowing through microchannels was experimentally found to grow with particle volume fraction, but not to depend clearly on the Peclet number. A crude model for the suspensions boundary layer at the wall, in which an excluded volume concept is combined with a viscosity that depends on concentration but not on shear rate, describes our experiments rather well.

5.6 Appendix

Appendix 5A:

Modelling of concentration profile (Φ) near the wall:

Fig. 5.6: (a) Schematic of a particle (diameter= $2a$) near flat wall. Here we changed the direction from y to z for clarity. (b) Theoretical profile of normalized particle volume fraction as a function of normalized distance from the wall calculated from eq. A8.

We consider the volume fraction in a slice with thickness dz at a distance y away from the wall (fig. 5.6), due to a suspension of spherical particles with radius a . The contribution from spheres located at distance y' away from the wall is given by:

$$d\Phi(y) = n(y')A dz = n(y') \pi (a^2 - z^2)dz \quad (5A1)$$

where $n(y')$ is the number density of particles at y' , A is the cross sectional area of the particle with the plane at y and $z = y' - y$. Hence the total volume fraction at distance y is given by:

$$\Phi(h) = \int_{-a}^a n(y+z) \pi (a^2 - z^2)dz \quad (5A2)$$

Ignoring layering effects near the wall we estimate $n(y)$ as:

5.6 Appendix

$$n(y) = n_{\infty} \quad \text{for } y > a \quad (5A3)$$

$$= 0 \quad \text{for } y < a \quad (5A4)$$

Where $n_{\infty} = 3\Phi_{\infty}/(4\pi a^3)$ and Φ_{∞} is the bulk volume fraction. Evaluating the integration for $y > 2a$ we indeed obtain:

$$\Phi(h) = n_{\infty} \pi a^3 \int_{-1}^1 (1 - x^2) dx = \frac{4}{3} \pi a^3 n_{\infty} = \Phi_{\infty} \quad (5A5)$$

Where $x=z/a$. For $0 < y < a$ we get:

$$\Phi(h) = n_{\infty} \int_{-a}^{y+a} \pi(a^2 - z^2) dy' \quad (5A6)$$

$$= n_{\infty} \pi a^3 \int_{1-y/a}^1 (1 - x^2) dx \quad (5A7)$$

So, the general expression of volume fraction becomes (eq. 5A5 and 5A7),

$$\Phi(y) = \Phi_{\infty} \left(\frac{y}{2a} \right)^2 \left(3 - 2 \left(\frac{y}{2a} \right) \right) \quad (5A8)$$

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Chapter 6

6 Dynamics of Colloids Confined in Microcylinders

We studied both global and local effects of cylindrical confinement on the diffusive behavior of hard sphere (HS) colloids. Using confocal scanning laser microscope (CSLM) and particle tracking, we measured the mean squared displacement (MSD) of 1 micron sized silica particles in water-glycerol. This combination of fluid and setup allowed to measure MSDs in a 4-dimensional parameter space, defined by the HS volume fraction (Φ : 0.05-0.39), cylinder radius (R : 2.5-20 micron), distance to the wall (z) and lagtime (τ : 0.03-60 s). MSDs measured over the entire cylinder confirm earlier findings that both ‘narrowing’ the cylinder and ‘populating’ it, cause a slower dynamics, in particular at high Φ . Additionally, decreasing R was found to cause a stronger ordering in the system, somewhat similar to the effect of increasing Φ . The effect of confinement on dynamics was further examined as a function of location. For the biggest cylinder, approaching the case of a flat wall, we found that an increase in Φ leads to a z -dependent MSD that shows a less pronounced decrease near the wall. Analyzing the radial (r) and azimuthal (θ) components, we found pronounced differences in the z -dependence that were ‘hidden’ in the total MSD. Near the wall, the r -MSD shows a much steeper z -dependence while at larger z , it shows a remarkable anti-correlation with the (peaked) local density $n(z)$. Also the dependence of the r -MSD on lagtime correlates with $n(z)$: diffusive in between the layers, but subdiffusive inside the layers. These observations bring earlier findings together, while also shedding new light on the diffusive dynamics of concentrated colloids in narrow capillaries.

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6.1 Introduction

Dynamics of colloids in confinement is of interest for both fundamental and practical reasons as the boundary and size-effects can alter material properties [1-3] and relaxation time(s) [4-6] (e.g. glass forming liquids) of a suspension, which in turn can influence the transport mechanism through narrow cavities [7, 8]. Confinement induced changes in dynamics can also be accompanied by alterations in the local structure of the fluid [5]. When subjecting a confined suspension to flow, both the structure and the dynamics are modified [9-12]; this is of relevance to micro- and nanofluidics [13] and nanotribology [14].

The present study is focused on the diffusive dynamics in the quiescent state. The most elementary way to provide confinement here, is via a single hard wall. Already this can significantly alter the dynamics of the colloids via potential (i.e. thermodynamic) and hydrodynamic interactions (HI). Slow-down of particle motion near a flat wall has been observed for several systems in the dilute limit. Extensions to the case of a curved wall have been explored, but the condition(s) where curvature starts to play an important role has not been mapped out in a systematic manner. Further extending from a curved wall into a full cylinder produces a new case, since apart from the curved interface also the overall confinement might also change the dynamics. For a large cylinder radius (relative to that of the particle), the interfacial effect should be similar to that of a single flat wall. However on making the cylinders progressively narrower, a transition from a local to a global confinement should be expected. Also the particle volume fraction should play a role here, considering that structure and dynamics generally become more strongly transmitted at higher concentrations. Remarkably, no systematic studies into the (combined) effects of cylinder radius and particle volume fraction have been done, not even for the case of hard spheres and hard walls.

The fact that the particle volume fraction is a key parameter in the dynamics of confined systems, is well established, and clear distinctions can be made between the dynamic regimes at different volume fractions. At low concentrations where the particles behave almost independent of each other, effects are mainly observed close to the wall(s), where displacements towards or away from the wall are strongly opposed by hydrodynamic forces. At higher concentrations but still below the hard-sphere glass transition, hydro-dynamic interactions between the particles modulate the effect of walls [15]. Not only the volume fraction but also the structure in the fluid then plays a role. At the very high concentrations of glass forming liquids, drastic slowdown of the diffusive dynamics has been associated

with correlated motions [16, 17] that become noticeable when the length scale of confinement becomes comparable to the cooperative length scale [18]. Also studies of colloidal suspensions in (quasi-) 2D systems [19-25] have demonstrated dynamical heterogeneities. Differences in particle mobility [26] may or may not be caused by differences in local structure.

In spite of these significant insights, a lot is still unknown about how confinement changes the (diffusive) dynamics. While the dilute limit has been considered theoretically [27, 28] and experimentally [29-34] by several researchers, and the same for the glassy state [6, 35, 36], for intermediate particle concentrations results are relatively scarce. In this regime, the diffusive dynamics is a result of an interplay between structure and hydrodynamics, where both are influenced by the confining walls.

Studies on the diffusive dynamics of moderately concentrated suspensions near a flat wall with light scattering [15, 37-39] showed that the wall effect gradually diminishes with increasing particle concentration. However optically no distinction could be made between different distances from the wall. It is therefore still not settled how the wall effect on particle dynamics is transmitted to the interior of the suspension and to what extent the influence will remain significant. In confinement by more than one wall, both the dimensionality and shape of the confining geometry also play a role. Confinement by two parallel walls [19-21, 23, 35, 40] provides a simple case, where particle motion was found to be restricted towards the wall. Confinement in an almost cylindrical capillary was considered [41] for a binary suspension. Very recently, also an extension was made to the role of the mechanical properties (softness or fluidity) [42, 43] of the confining material.

In this work we consider the case of hard sphere colloids confined by cylindrical hard walls. Based on the reviewed literature, two general trends are expected also in our case: i) narrowing down the confinement should lead to a slower (average) dynamics of the particles. This slowing down should become more drastic at higher volume fraction. ii) confining walls have a layering effect, i.e. the highest local concentration of particles should occur at the wall. Specific new aspects that will be considered here, are: 1) the transition from the local confinement by one wall, to a global one that corresponds to the entire cylinder, 2) the dependence of this transition on particle volume fraction and 3) local variations in the dynamics, considering both the distance from the wall, and the (radial and azimuthal) directionality of the motion.

6.2 Experiments

6.2.1 Sample preparation

We synthesized [44-46] core-shell silica spheres of 1.0 μm diameter (polydispersity $\approx 5\%$) containing a core of 500 nm diameter labelled with Fluorescein isothiocyanate (FITC) to allow detection of the centre of mass of each particle accurately, even at high concentrations. These colloidal probes were suspended in water-glycerol mixture (18:82 by weight, solvent mass density $\rho_s = 1.21\text{ g/ml}$) to achieve near refractive index matching with the silica spheres ($n_p = 1.46$), thus minimizing the scattering of light. Suspensions of different volume fractions were prepared by diluting a stock solution of particle volume fraction $\Phi = 0.45$. The method of the sample preparation is described in ref. [10]. We also added 0.8 mM LiCl to the suspension to screen the surface charge; the corresponding calculated electrical double layer thickness [47] was about 8 nm. This should be sufficiently short-ranged to make a nearly HS system in water-glycerol. The theoretical settling speed of silica spheres (mass density $\rho_p = 1.89\text{ g/ml}$) is less than 10 nm/s in the dilute limit, and expectedly about 10 times slower at $\Phi \approx 0.3$ [48]. Considering the height of the cylinders (24 μm) and the total time lapse between the filling of the channel and the last experiment (800 s), this means that changes in suspension concentration (at the focal plane) can be neglected. Five particle volume fractions ($\Phi = 0.05, 0.28, 0.32, 0.35$ and 0.39) were prepared.

6.2.2 Microfluidics

Microcylinders of different diameters were designed embedded in the side walls of the microchannels as shown in Fig. 6.1a. Molds made from SU8, were fabricated on silicon wafers by soft lithography, and subsequently transferred to channels by negative stamping in poly (dimethylsiloxane) (PDMS). We mainly used 30 μm (width) $\times$ 24 μm (height) $\times$ 1 cm (length) PDMS channels bonded onto a 170 μm thick glass cover slip, after making them hydrophilic using Oxygen plasma for 50 s at 100 W. Since the hydrophilicity of the PDMS can last for nearly 200 h [49], and sticking of particles onto the channel walls had to be avoided, we waited at least two weeks before using the channels. Both ends of the microchannel were connected with reservoirs to allow pressure control without problems due to solvent evaporation. The connections between the microcylinders and the channel consisted of rectangular necks with a length of at least 10 μm and a width of 3 μm (smallest cylinder) to 6 μm (largest cylinder); these dimensions were appropriate to

6.2 Experiments

ensure absence of flow inside the cylinders during the measurements. Cylinders were filled directly with the suspension. As soon as the particles had reached the outlet, the second reservoir was connected, and the hydrostatic pressures balanced, and a waiting time of 5 min was given. Fig. 6.1b shows a snap shot of a microcylinder filled with 1 μm sized silica spheres. All experiments were performed at 22 ± 1 $^{\circ}\text{C}$.

Fig. 6.1: a) Schematic of the experimental setup. Microcylinders are embedded in the side of the microchannel of 1 cm long, 30 μm wide and 24 μm high. Diameters are 40 μm , 20 μm , 10 μm and 5 μm . b) Confocal image of a suspension at volume fraction 0.28, taken 12 μm above the bottom. Scale bar: 10 μm .

6.2.3 Imaging by Confocal Microscopy

We use a VisiTech ‘VT-infinity³’ Confocal Laser Scanning Microscope (CSLM) to visualize the motion of the colloids. The microscope is connected to a Hamamatsu digital camera (ORCA-flash 4.0) and a 488 nm laser source. To obtain the best spatial resolution for particle localization, we used a 100X oil immersion objective with 1.3 numerical aperture. This resulted in a field of view of 65 $\mu\text{m} \times 75 \mu\text{m}$ and an effective pixel size of 130 nm. The focal plane was set at the mid plane ($H = 12 \mu\text{m}$) of the microchannel structure, to minimize the influence of the top and bottom walls on the particle dynamics. Considering the finite field of view, cylinders were recorded one by one, except the smallest two which were imaged simultaneously. For each concentration, typically 5000 frames were recorded at a

rate of 30 fps. We also imaged the suspensions in bulk at the same concentration and height inside a cuvette to compare with the particle dynamics inside confined cylinders.

6.3. Data analysis

Standard particle tracking software [50, 51] was used to localize and track particles. Since our video recordings had a duration of ≈ 150 s per cylinder, and the particle dynamics needed to be precisely resolved with respect to distance from the wall, correction for table drift was essential [9]. The average drift velocity (calculated from particle trajectories) was typically 2 nm/s, corresponding to a total cylinder displacement of ≈ 300 nm per recording. Over plotting the (drift corrected) particle coordinates of the entire movie resulted in images like Fig. 6.2a and 2b. Measuring the axis location (and radius) of the cylinder from the contour then allowed a coordinate transformation from (x,y) to (r,θ) for each particle position: $r^2 = x^2 + y^2$ and $\theta = \tan^{-1}(y/x)$. The availability of θ coordinates was then used to exclude all particles with θ values that occurred within 15 degrees from the neck of the cylinder. The remaining data were used to assess the accuracy in the measured cylinder radius, by inspecting $r(\theta)$ plots as in Fig. 6.2c. Depending on the particle volume fraction and cylinder radius, the inaccuracy varied between 0.5 and 1.0 pixel (65-130 nm), *i.e.* about 2 times the standard deviation of the particle size distribution. Since r corresponds to the radial position of a particle centre, the physical radius R of the cylinder was obtained by adding one particle radius (500 nm) to the ‘maximum detected radius’ indicated by the dashed line in Fig. 6.2c.

6.3. Data analysis

Fig. 6.2: Measurement of the center location and radius of the cross section of the cylinder, for the experiment at $\Phi = 0.28$ and $R = 20 \mu\text{m}$. (a) time projection of all (drift corrected) particle center coordinates. (b) zoom in, also comparing the non-corrected (black) and drift-corrected (green) coordinates. (c) same data as in Fig. 6.2b but now plotted as r vs θ . The neck occurring around $\theta = \pi/2$ has been left out.

6.3.1 Concentrations

Local particle concentrations were calculated as a function of r by counting the number of detected particles in a ring with radius r and width Δr and normalizing for the area of the ring:

$$n(r') = N_p(r') / \left[(\theta_{max} - \theta_{min})(r' + \frac{1}{2}\Delta r) \right] \quad (6.1)$$

where $N_p(r')$ is the number of particles found for $r' < r < r' + dr$ and $\theta_{min}, \theta_{max}$ indicate the angular range over which was integrated. dr is the width of the r -bin, which was set equal to 50 nm. It should be noted that N_p depends on the selection criteria used in the preceding image analysis step. Accordingly, in our 3D system where the distance of a particle to the focal plane follows a distribution, the measured number of particles per unit area $n(r)$ does not have a simple meaning. However, given that the illumination conditions and camera settings were the same, $n(r)$ should be proportional to the local volume fraction.

6.3.2 Mean Squared displacements

In the calculations of spatially resolved MSDs, the transformation to polar coordinates was applied to the center of mass (x_{CM}, y_{CM}) of each trajectory, after which r_{CM} was used to assign a specific r -bin to the considered trajectory. For all particle volume fractions and cylinder radii, the total r -range was binned with a Δr of 0.13 μm . Considering that the typical MSD at a lagtime of 100 s lies between 0.01 and 0.1 μm^2 (see Fig. 6.4), this choice should be appropriate: although some particles visited other r -bins than they were assigned to, the ensuing ‘smearing’ of the r -dependent MSDs should be small.

Decomposition of the (local) MSDs in the radial (r) and azimuthal (θ) directions was done using the θ coordinate of the center-of-mass of each individual trajectory. Using this θ_{CM} , each individual displacement (vector) $\Delta \vec{s}$ of the particle was split into Δs_r and Δs_θ :

$$\Delta s_\theta = \Delta \vec{s} \cdot \vec{e}_\theta \text{ and } \Delta s_r = \Delta \vec{s} \cdot \vec{e}_r \quad (6.2a)$$

with

$$\vec{e}_r = \cos \theta_{CM} \vec{e}_x + \sin \theta_{CM} \vec{e}_y \text{ and } \vec{e}_\theta = -\sin \theta_{CM} \vec{e}_x + \cos \theta_{CM} \vec{e}_y \quad (6.2b)$$

Here $\vec{e}_r$ is the unit vector in the direction of r_{CM} , while $\vec{e}_\theta$ points in the perpendicular direction that makes θ increase. $\vec{e}_x$ and $\vec{e}_y$ are the unit vectors in the x and y directions. While this decomposition ensures that the length of $\Delta \vec{s}$ is conserved in all coordinate transformations (also the ones involving multiple steps), some ‘cross-bleeding’ between the displacements in the r and θ directions occurs, if the average location of the particle in the given displacement step, does not fall on the line that runs through the origin (*i.e.* the center of the circle) and (x_{CM}, y_{CM}). This error, which is illustrated in Fig. 6.3, is largest near the origin,

6.3. Data analysis

where the distinction between r and θ directions is least important. Close to the wall, the error is small.

Fig. 6.3: Illustration (not to scale) of the approximation made in the decomposition of individual displacements into radial and azimuthal directions. r_{CM} and θ_{CM} indicate the center-of-mass location of a trajectory (most steps of which are not shown). Individual displacement steps Δs (like the one in black) are decomposed into the radial and azimuthal directions, belonging to r_{CM} (dashed blue lines). The actual r and θ directions (red dashed lines) are slightly different.

Mean Squared Displacements (for an individual trajectory) in the r and θ directions were then calculated after introducing new arrays to represent the (lag)time dependent displacement of a single particle i :

$$S_r(i, j) = S_r(i, 0) + \sum_{k=1}^j \Delta s_r(i, k) \quad \text{for } j = 1 \text{ to } N_j \quad (6.3)$$

$$S_\theta(i, j) = S_\theta(i, 0) + \sum_{k=1}^j \Delta s_\theta(i, k) \quad \text{for } j = 1 \text{ to } N_j \quad (6.4)$$

where j indicates the time step (N_j is the number of steps of the trajectory). These new arrays were then analysed for the entire set of trajectories by the standard routine for calculating MSD (components) [48], as if they were x and y coordinates. Finally, for the purpose of analysing the MSDs as a function of distance to the wall (z), the r_{CM} label of each trajectory was transformed into a z -label via $z = R - r_{CM}$. Plotting MSDs versus z allows to compare between cylinders having different radii.

6.4 Results and discussion

6.4.1 Global MSDs

Lagtime-dependent MSDs were measured for 4 volume fractions ($\Phi = 0.05, 0.28, 0.35$ and 0.39) and 5 degrees of confinement ($R = 2.5, 5, 10, 20 \mu\text{m}$ and ∞ , i.e. bulk fluid). The data for bulk fluids (shown in Appendix A) show similar behaviour to earlier findings for colloidal hard spheres [17, 19, 52]: on increasing Φ , the MSD gets smaller, while the lagtime dependence become subdiffusive. These changes in MSD magnitude and signature are minor at low Φ (< 0.1) but show a strong dependence on volume fraction for $\Phi > 0.3$.

Fig. 6.4: Lagtime-dependent MSDs for bulk and confined fluids at different volume fractions ($\Phi = 0.05$: lines and $\Phi = 0.39$: solid symbols). Cylinder diameters: $40 \mu\text{m}$ (red); $20 \mu\text{m}$ (green); $10 \mu\text{m}$ (dark yellow); $5 \mu\text{m}$ (blue). Black line and symbols represent bulk MSDs. MSDs for $\Phi = 0.05$ have been multiplied with 5 for clarity. Dashed line is of slope unity and open circles (magenta) indicate the noise floor.

Increasing the confinement while keeping Φ constant, results in similar trends. As shown in Fig. 6.4, reducing R from ∞ to $2.5 \mu\text{m}$ has a modest effect on the MSD at $\Phi = 0.05$, while at $\Phi = 0.39$ the MSD clearly becomes sub-diffusive, especially for the two smallest R (intermediate volume fractions not shown). Considering the data at $\Phi = 0.05$, the MSDs of the bulk fluid show a remarkable difference with those of the confined fluids. This is ascribed to the strong local effect of the cylinder wall: in the limit of low Φ , a strong reduction in diffusion coefficient takes place in the first 2 particle layers near the wall [29]. These two layers makes a relatively strong

contribution to the average MSD for the whole cylinder. As we will show, at $\Phi = 0.39$ the effect of the nearby wall on the local MSD is less strong; this explains why at this volume fraction the data at $R = 20 \mu\text{m}$ and those for $R \rightarrow \infty$ are closer to each other.

Fig. 6.5: total MSD as a function of particle volume fraction confined in different cylinders. MSD for each concentration inside different cylinders is measured at lag-time $\tau = 2.0 \text{ s}$. Different symbols (and colors) are for different cylinder diameters (dcyl): $40\mu\text{m}$ (red circle), $20\mu\text{m}$ (green upper triangle), $10\mu\text{m}$ (blue lower triangle), $5\mu\text{m}$ (pink diamond). Black square belongs to the respective bulk MSDs.

In Fig 6.5 we illustrate these trends, by intersecting the data as in Fig. 6.4 at a representative lagtime of 2 s, and plotting the MSD magnitude vs. volume fraction. Now including all Φ , we find that the effect of cylindrical confinement on the MSD is more drastic at higher volume fractions (taking into account the previous remark about the data point at $\Phi = 0.05$). Also this trend corresponds well to earlier findings for colloidal HS, albeit that most of these were made in plate-plate geometries [19, 23]. It thus appears that at the level of the total MSD (i.e. neither distinguishing between locations, nor between the directions of the diffusive motion), the difference between confinements by cylinders or by flat plates is modest.

In several previous studies, these trends were interpreted as ‘confinement induced freezing’. While our experiments do not really reach the ‘freezing’ regime, the trends are similar to e.g. work of Eral *et al* [19] who also found the beginning of subdiffusive behaviour in bulk between $\Phi = 0.37$ and 0.42 , and significant

confinement effects for $\Phi > 0.33$, leading to MSD plateaus under extreme confinement. An exploratory experiment performed by us at $\Phi = 0.45$ and $R = 2.5 \mu\text{m}$ also showed a lagtime independent MSD (data not shown). This gives further confirmation that ‘confinement induced freezing’ is also found in cylinders.

Fig. 6.6: Comparison of number density $n(z)$ as a function of distance from the wall for two representative volume fractions. Cylinder diameters: $5 \mu\text{m}$ (black), $10 \mu\text{m}$ (red), $20 \mu\text{m}$ (green), $40 \mu\text{m}$ (blue). Data for the central areas of the cylinders are have been left out because of insufficient accuracy.

We extend our analysis by considering how the structure in the fluid is influenced by the confinement. Fig. 6.6a and b show how the number of particles per unit area depends on the distance to the cylinder wall, for different cylinder radii. For both $\Phi = 0.28$ and 0.39 (and also at the intermediate Φ values), $n(z)$ shows a strong peak at the wall (regardless of cylinder radius). This observation agrees well with earlier theoretical [35, 53-56] and experimental studies [23, 57-59] where walls with a curvature radius much bigger (∞) than the particle radius, were found to have a strong layering effect. Also the increase in sharpness of the (first) concentration peak with the overall Φ corresponds with earlier findings.

Interestingly, the data in Fig. 6.6 also show a clear effect of increasing confinement on the structure of the fluid in the entire cylinder. As R is reduced, the $n(z)$ profiles become more pronounced, indicating that the ordering in the fluid increases. This is best visible in Fig. 6.6b for $\Phi = 0.39$: the peaks in $n(z)$ get higher, while the minima become lower. For the two smallest cylinder radii, the ordering is even preserved over the entire z -range (while it vanishes at large z for the two largest cylinder radii). We remark that this confinement-induced ‘transmission’ of

6.4 Results and discussion

the order in the fluid, appears to be significantly stronger than in a previous study where two horizontal flat plates were used to confine the colloids [19]. This difference might be due to the alignment of the z -direction with gravity, and/or the fact that one wall had a significant roughness in the previous work (in the present study, the entire wall is smooth while the in-plane distribution of particles is not influenced by gravity).

Fig. 6.7: Comparison of number density $n(z)$ as a function of distance from the wall for different concentrations (at fixed cylinder diameter). Volume fraction (Φ): 0.28 (black), 0.32 (red), 0.35 (green), 0.39 (blue).

Since the confinement-induced ordering might bear similarity to the effect of increasing the overall particle volume fraction, it is interesting to consider Fig. 6.7, which shows $n(z)$ as a function of Φ for two representative cylinder radii. Even when taking into account that the peaks will be higher, partly because of the higher Φ , it is clear that the degree or order (the relative magnitudes of the maxima and minima of $n(z)$) is increased. The similarity between the effects of increasing confinement and increasing particle concentration on the structure in the fluid has not been demonstrated earlier as far as we know. It could indicate that (in our case) ordering plays a slightly different role in the slowing down of the particle dynamics via spatial confinement. The argument that spatial confinement shifts the glass transition to lower volume fractions is generally associated with the concept of hydrodynamic clusters, which does not assume a certain order.

6.4.2 Local MSDs

We now examine the effects of the spatial confinement on the MSD at different locations inside the cylinder. In previous works, diffusion coefficients (and for more concentrated systems MSDs) have been measured as a function of distance to the wall [20]. In the limit of low Φ , particle tracking experiments by Eral *et. al.* [29] showed that their $D_r(z)$ and $D_\theta(z)$ that were similar to predictions by Brenner for a particle near a single flat wall [27]. Small differences could be attributed (almost quantitatively) to effects of wall curvature and the presence of end-surfaces. Michailidou *et. al.* [15, 38] studied more concentrated systems near a single wall, using a Dynamic Light Scattering technique. Our data allow extension of these works by measuring MSDs in concentrated fluids as a function of distance to the wall.

For $R = 20 \mu\text{m}$, the difference between MSD in the heart of the cylinder and the bulk MSD is modest. This suggests that close to one wall, the contributions of all other walls might be negligible. Since $R \approx 20a$, the curvature might be negligible, in which case we could almost translate the results to that of particles near single walls. Fig. 6.8 shows (for all Φ) the z -dependent magnitude of the MSD at a lagtime of 2.0 s; the choice for this lagtime is not critical, since the MSDs are still (nearly) diffusive for $R = 20 \mu\text{m}$ (see Fig. 6.4). Comparison of the MSDs in the central area of the cylinder ($R > 3 \mu\text{m}$) with their corresponding values in bulk fluid, reveals that –except for $\Phi = 0.39$ – the global effect of confinement is relatively small (compared to the changes in MSD as the wall is approached). This provides reasonable justification for comparing the results with the dynamics of suspensions near single (and flat) walls. We observe in Fig. 6.8 that as Φ is increased, both the structure in the MSD and the range over which it steeply decreases as the wall is approached, become smaller. This suggests a stronger hydrodynamic screening, *i.e.* in the particle dynamics the presence of the wall gets increasingly masked by the (dense suspension of) particles near the wall. Another observation in Fig. 6.8 is that whereas at low Φ the MSD increases gradually on moving away from the wall, as the volume fraction gets higher, also some ‘structure’ becomes visible in the z -dependent MSD. This aspect will be discussed in more detail below.

Fig. 6.8: Total MSD (at lagtime 2.0 s) as a function of distance from the wall in fixed cylinder for various particle concentrations. Different colour corresponds to the different particle volume fraction (Φ): 0.05 (black), 0.32 (red), 0.35 (green), 0.39 (blue). Dashed lines are the respective bulk MSD values. Cylinder radius = 20 μm .

6.4.2.1 Differences between radial and azimuthal components

We deepen our analysis by decomposing the MSD into the radial and azimuthal directions (calculated as explained in Sec. 2). From these data, shown in the lower panel of Fig. 6.9, it becomes evident that strong differences exist between the two components: while the azimuthal MSD only shows a clear z -dependence very close to the wall in the cylinder with $R = 20 \mu\text{m}$, the radial MSD clearly shows several local minima and maxima in both cylinders. For $z < 1 \mu\text{m}$, the decrease of the radial MSD is much stronger than that of the azimuthal one. This also means that the diffusion becomes strongly anisotropic near the wall. This is in qualitative agreement with the diffusive dynamics of a single particle near a flat wall [30-32, 34, 60]. For $z > 3 \mu\text{m}$ the radial and azimuthal MSDs become equal; this coincides with the z -range where $n(z)$ becomes nearly constant for $R = 10$ and $20 \mu\text{m}$ (it thus appears that as the structure is lost, also the anisotropy of the diffusion disappears). It is also interesting to examine the role of the cylinder radius. As R is decreased from 20 to 10 μm , both MSD components near the wall show less reduction relative to their values in the central region of the cylinder. This suggests that the increased confinement provides an effect that is similar to the increased

hydrodynamic screening when Φ is enhanced. Besides that, a small decrease of the MSD plateaus is found when R is changed from 20 to 10 μm . This illustrates the effect of global confinement.

Fig. 6.9: Radial and azimuthal MSD values (at lagtime 2.0 s, lower graphs) compared to local particle concentrations (upper graph) for the fluid with $\Phi = 0.39$ in the cylinders with $R = 5 \mu\text{m}$ (left), $10 \mu\text{m}$ (middle) and $20 \mu\text{m}$ (right). Blue and red lines indicate MSDs in the radial and azimuthal directions respectively.

Interestingly, comparing the z -locations where (especially the radial) MSDs have local minima and maxima with those in the concentration profile $n(z)$, reveals an anti-correlation: ‘less crowding’ (a lower n) corresponds to a higher ‘diffusivity’ (a higher MSD). Eral et al [19] measured both number densities and MSDs as a function of distance to the (smooth) wall. They did not report an anti-correlation, but their MSDs were measured in optical planes that were parallel to the walls. This would ‘translate’ to the azimuthal direction in our experiments, where the anti-correlation is much weaker as compared to the radial direction.

6.4.2.2 Lagtime dependence

Another interesting aspect of the dynamics concerns the diffusive signature of the local MSD, *i.e.* the lagtime dependence of the MSD for a given z -coordinate. This dependence is generally difficult to measure, since it requires trajectories that are

on one hand long enough to obtain a broad range of lagtimes, but on the other hand cover a spatial range that is small enough to allow accurate assignment of a z -location to a trajectory. The combination of our particle size and solvent viscosity, turns out to be ideally suited for our purpose: even at the smallest lagtime of 0.03 s, the diffusive displacement is still large enough to be measured (see Fig. 6.4) while lagtimes up to 8 s are still small enough to prevent either significant loss of particles from the focal plane, or significant changes in z (the latter can be verified from the MSDs in Fig. 6.4 by taking the square root).

Fig. 6.10: (a) local number density $n(z)$ of particles as a function of distance from the wall. This data corresponds to $\Phi = 0.39$ inside the largest cylinder ($d_{\text{cyl}} = 40\mu\text{m}$). (b) MSD in the radial direction as a function of lag time τ . The colors in both panels correspond to each other. Note that the data at $\tau = 2.0$ s are also shown in Fig. 6.9

Analysis of the MSDs at $\Phi = 0.39$ in the cylinder with $R = 20\mu\text{m}$ revealed that, while the azimuthal MSDs only show a significant change in amplitude very close to the wall (shown in Fig. 6.9), and little change in diffusive exponent (data not shown), the time-dependent radial MSD shows strong variations in both magnitude and ‘diffusive exponent’. As shown in Fig. 6.10, both quantities oscillate around a

‘mean value’ that is ultimately reached as z starts to exceed $3 \mu\text{m}$. Comparison of the MSD with the local concentration shows that where $n(z)$ has a local maximum, the r-MSD is more strongly subdiffusive, while at local minima of $n(z)$ the r-MSD is more diffusive. After the first 3 peaks, this correlation weakens and the noise level of the MSD increases (due to the smaller area of the ring in the cylinder). For the layer directly adjacent to the wall, the lagtime-dependent r-MSD starts with a (sub) diffusive signature but then reaches a plateau. This indicates that the radial motion is effectively confined to a ring, which in the particular case has a width of ≈ 0.1 particle diameter. This radial confinement aspect, together with the strong anisotropy of the local diffusive displacements, is illustrated (now for a cylinder with $R = 5 \mu\text{m}$) by Fig. 6.11.

Fig. 6.11: Two dimensional trajectory plots (i.e. time projections of displacements by the same particle) for the fluid with $\Phi = 0.35$ inside a cylinder with $R = 5 \mu\text{m}$. Integration time is 160 s. Trajectories are distinguished via their color. Distance units are given in μm .

6.5 Conclusions

This study both corroborates and extends on earlier findings on the dynamics of confined suspensions. At low concentration we recovered the strong effect of the (most nearby) wall, giving a strong reduction in the diffusion coefficient, in particular in the radial direction. Also the global trend that the diffusive dynamics slows down as the confinement length (in our case the cylinder radius) is diminished, was reproduced by our experiments. Several new insights for monodisperse hard sphere fluids were obtained by extending the experiments in

microcylinders to a broader range of both cylinder radii and particle volume fractions.

Experiments in the biggest cylinder, approaching the case of a flat wall, allowed to study how both the ‘parallel’ and the ‘perpendicular’ diffusion change as the fluid becomes more concentrated. Firstly, the relative reduction in MSD near the wall (as compared to the center of the cylinder) becomes weaker. This is ascribed to a stronger hydrodynamic screening, due to the higher abundance of other particles between the probe and the wall. Secondly, the increase in diffusivity on moving away from the wall is no longer continuous; local minima and maxima are found to develop as the volume fraction is increased. This phenomenon, which is related to the formation of a layered structures, applies in particular to the radial (‘perpendicular’) MSD, whose lagtime dependence shows a clear subdiffusive behavior for particles inside layers. Accordingly, the anisotropy in the particle dynamics at the wall is preserved.

For concentrated suspensions, reduction of the cylinder radius has several consequences. Since the effects of local (wall) and global (cylinder) confinement become increasingly intertwined, attribution of the observations to a single cause becomes increasingly difficult. The slow-down of the overall dynamics was also found earlier, and is broadly recognized as a global confinement effect. Our additional observation that the dynamics becomes spatially more homogeneous could be seen as the result of an increased dominance of the global confinement effect. However the fact that this more homogeneous dynamics occurs in spite of a more heterogeneous structure (increased ordering) in the fluid (as show in Fig. 6.9) is remarkable. It illustrates that the relation between confinement, fluid structure and hydrodynamics is a complex one which still needs to be further understood.

6.6 Appendix

Appendix 6A

Fig. 6.12 (color online): Total MSD (μm^2) vs lag time (s) of colloids in bulk suspension for different particle concentrations. Solid symbols indicates different volume fractions (Φ): 0.05 (black square), 0.28 (red circle), 0.35 (green upper triangle), 0.39 (blue lower triangle). Open circle (violet) indicates the noise floor generating from the mechanical vibration of the microscopic stage. Solid black line is the theoretical prediction of Brownian diffusion in similar suspension of infinite dilution. The dashed line has a slope of unity to indicate the free motion of a particle.

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Chapter 7

7 Conclusions and outlook

This chapter summarizes the most important findings presented in this thesis. The diffusive dynamics of monodisperse hard-sphere colloids, in microchannel flow and in cylindrical confinements, formed the main part of the research. To measure anisotropic and location-dependent diffusive behaviours, sometimes also superimposed on flow, new analysis methods had to be developed. Novel developments on the experimental side were the use of well-defined microfluidic channels with cross sections of 20-30 μm and confining cylinders with radii as small as 2.5 μm , for studies on concentrated suspensions. At the end of this chapter we will provide some ideas for possible future extensions of this work.

7.1 Conclusions

7.1.1 Particle tracking in non-uniform flow

In many particle tracking experiments, a correct identification of the far majority of particle trajectories, *i.e.* keeping the percentage of misidentified trajectories well below 1%, is a general requirement. The case of colloidal suspensions flowing through microchannels presents an appreciable challenge, especially if the flowrate and shear gradients are high, and even more so if the property of interest is the Mean Squared Displacement function. Chapter 3 presents a method for reliable particle tracking in non-uniform flow fields with superimposed Brownian motion. Use of an iterative scheme in which the flow velocity profile becomes more accurate per iteration step, and local advective motion is subtracted per time step, proved to be successful. Validation of the method using simulation data confirmed for volume fractions up to 0.4, and in a wide range of normalized flow rates and diffusion coefficients, that input diffusion coefficients were measured with acceptable accuracy. It is explained in chapter 3 how the advection can be decoupled from Brownian diffusion. We also demonstrate that to quantify particle dynamics in terms of diffusion coefficients, it is necessary to remove lateral motion and drift mixed with Brownian diffusion. We have implemented this technique to quantify shear induced diffusion in microchannel flow.

7.1.2 Shear and wall effect on Brownian diffusion

Shear induced diffusion is a well-known phenomenon for non-Brownian suspensions, but less so for colloidal fluids, where also thermally driven Brownian motion plays a role. In chapter 4, we examined shear induced diffusion of colloidal suspensions as a function of the Peclet number (which compares the timescales of diffusion and convection). Diffusion coefficients of colloids were measured in a pressure driven flow by tracking the motions of individual particles, thereby taking into account the aspect of spatial variation along the channel cross-section (since the flow profile was roughly parabolic). Also the wall effect on diffusion in presence shear was quantified (for the first time). Our experimental results show a gradual transition from thermal to shear induced diffusion. The apparent particle diffusivity, defined from the residual motion (also the effect of Taylor diffusion is removed) increases significantly in dense suspensions where particles frequently collide with each other due to the velocity gradients. This enhanced diffusion occurs in both the flow and the velocity gradient directions, but is strongest in the

flow direction. Hence in concentrated systems, the diffusivity is minimal near the channel centre (where the shear rate is zero). Maximum diffusivity is reached near the walls where the shear rate is highest. However, very close to the wall (within two to three particle diameters) the diffusion coefficient reduces strongly, irrespective of particle concentration. This indicates that ultimately the wall effect dominates over the shear effect.

7.1.3 Role of particle concentration on apparent slip

The occurrence of apparent wall-slip in hard sphere suspensions, and its dependence on particle volume fraction (Φ) are discussed in chapter 5. In such systems, wall slip might be expected as a result of the depletion of particulate matter near the wall. Measurement of the velocity profiles revealed slip velocities that are linearly progressive with the applied shear rate. Defining the apparent slip length (β) by extrapolating the flow velocity profiles to zero, we found that β is only weakly dependent on the shear rate. However, considering the dependence on particle concentration, we found a clear and gradual increase of β with Φ , tending towards an asymptotic behavior for $\Phi > 0.3$. A simple theoretical model in which the particle depletion near the wall is described with a purely geometric argument, and combined with an empirical expression for the volume fraction dependent viscosity, matches well with our experimental results which confirms the role of particle concentration and depletion on apparent slip during the flow of particulate suspensions.

7.1.4 Colloidal dynamics: effect of particle concentration and confinement

The influence of spatial confinement on the diffusive dynamics of colloidal hard spheres has previously been reported in the dilute limit for particles near flat walls or confined by curved objects such as cylinders. Concentrated suspensions under confinement provide a strongly different case. Experiments on confined suspensions, mostly between two (quasi) parallel plates, had shown that the glass transition shifts to lower concentration. Also simulations on cylindrical confinement had indicated this trend. However, details of this confinement-induced transition had remained unclear.

To shed more light on the phenomenon, we examined the effect of cylindrical confinement on the structure and diffusive dynamics of monodisperse suspensions, covering a range of cylinder radii (2.5 - 20 μm) and particle volume fractions (0.05-0.39). Our study shows that a strong interplay between confinement and dynamics occurs for $\Phi > 0.28$. The earlier observed global trend towards a glassy state was confirmed. Additionally, we found that a clear layering of the particles takes place along the curved interface, and as the cylinder is made smaller the structure gets even more pronounced. Diffusion in the radial direction was found to be anti-correlated with the local particle density, most clearly for the particle layer in contact with the wall. Diffusion in the azimuthal direction remained almost independent of the structure. Accordingly, a strong anisotropy in particle dynamics is observed near the wall. Further investigation of mean squared displacement in radial direction reveals that the motion is sub-diffusive in the layered structures and near-diffusive between the layers.

7.2 Outlook

The works presented in this thesis provide some key understanding about the dynamics of colloids in equilibrium and non-equilibrium conditions. These findings also open up some new opportunities to continue research in similar systems to address some interesting and unsolved fundamental questions. Few of those are mentioned in this section.

7.2.1 Mixing of colloids in microchannel flow

So far it has been observed that when a dense particulate suspension flows through a channel at high speed (i.e. Peclet number), particles tend to migrate towards the channel centre and generate a concentration gradient along the channel cross-section with a peak near the centre [1-4]. This issue could be mitigated with counter-measures like applying acoustic waves or electric fields. Acoustic waves are generally used to align particles in a streamline for dilute suspensions [5] in microchannel flow, but in concentrated suspensions it can produce much more elegant situations[6]; for example it can assist rigorous mixing of particles and form new structures. Electrowetting could also help mixing different components in microchannel flow.

7.2.2 Complex colloids in microchannel flow

The flow experiments in this thesis were dedicated to the dynamics of hard sphere colloids; a reference system that can be characterized by the minimum number of parameters: particle radius, volume fraction and Peclet number. In practice, a variety of different types of colloids is encountered, both in the research lab and in applications. Several of those have not yet been studied as (concentrated) suspensions in microchannel flow. Even if only one property would distinguish them from pure hard spheres, differences in the concentration and velocity profiles as well as in the diffusive behaviour should be expected. Anisotropic particles like plates and rods for example, show rotational diffusion, which can be suppressed by flow and walls. At high concentration also the equilibrium phase behaviour (involving collective orientation) should come into play. Soft compressible particles such as polyNIPAM [7] could be compressed in flow, leading to a jammed state that might either clog the channel, or flow like a plug. The distinction between the two scenarios would probably be set by the strength and nature (attractive or repulsive) of the particle-wall interactions. Considering the many possible ways for modifying the physico-chemical properties of both the particles and the walls, the behaviour of suspensions in flow might be as rich as their phase behaviours at rest.

7.2.3 Roughness effect on depletion and flow profiles of Brownian suspensions

In Chapter 5, we inspected the relation between particle concentration and apparent slip length, and connected it to a depletion effect. So far, it is unclear how the wall roughness influences the depletion of colloids and apparent slip length. Roughness should influence the flow profile of colloidal suspensions, but details are still unknown. Presence of wall roughness close to particle length scale may help to suppress the slip and might make it easier to measure rheological properties of viscoelastic materials. In case of microchannel flow, it will also be interesting to inspect the effect of wall roughness on flow profiles in narrow channels.

7.2.4 Diffusive dynamics in square confinement

Another interesting extension could be the study of colloidal dynamics in square cavities, shown in fig.7.1. Intuitively, the corner effect will be stronger than the effect of a single side wall and simultaneously the contributions from all the walls will be same at the centre. Though, it could be little bit complex to explain the results but still might be interesting to inspect the glass transition in these kind of geometries.

Fig. 7.1: CSLM image of a suspension $12\mu\text{m}$ from the bottom plane inside a square cavity. Length of each side is $40\mu\text{m}$. Scale bar = $10\mu\text{m}$.

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Summary

The work presented in this thesis focuses on the diffusive dynamics of colloids in pressure driven flow near a wall and confined in microcylinders. As part of this, a method to accurately measure the diffusion coefficients in presence of an inhomogeneous shear field was developed. Additionally, it is examined in this thesis how the apparent wall slip of a Brownian suspension flowing through a microchannel changes with the particle concentration.

Measurement of the diffusion coefficients of a colloidal particle in flow is quite complicated especially in pressure driven flow inside a microchannel, as the Brownian diffusion is superimposed with an advection pattern. Before the diffusion coefficients can be measured, the advection needs to be carefully decoupled from the Brownian motion. **Chapter 3** deals with this problem and illustrates a novel method to separate the stochastic particle motion from the non-uniform background flow. Validation of this technique with computer simulations establishes the reliability of this method for particle volume fractions up to 0.4. This method requires particle coordinates over time as input and measures all individual particle displacements iteratively. In each iteration, the measured average velocity profile is used to subtract the advective displacement of each particle per individual time step. After the final iteration, mean squared displacements of the colloids are measured from the residual trajectories. This method works well for dilute as well as for concentrated suspensions.

Shear induced diffusion is a well-known phenomenon. However most studies were not focused on colloidal particles, in spite of their practical relevance. It was also yet unclear how an inhomogeneous shear field influences the dynamics of colloids. In microchannel flow, the local shear rate gradually changes along the channel cross-section. This can alter the particle motion and the local structure of the suspension. Simultaneously, the confining boundaries which set up the flow, exert their own influence on the particle dynamics. Experiments shown in **Chapter 4** reveal that the diffusion of colloids in presence of shear strongly depends on the hydrodynamic interactions between the particles. In dilute systems where the particles hardly interact, the inherent diffusion coefficient is isotropic, and independent of the local Peclet number (a dimensionless shear rate). In contrast, for dense systems (strong particle interactions via hydrodynamics), the colloids show a

transition from thermal to shear induced diffusion at Peclet numbers around one. Shear enhanced diffusion occurs in both the flow and the velocity gradient directions, but is strongest in the flow direction. Another clear observation is the reduction of diffusion coefficients near the wall, although the local shear rate is maximum there. Hence in concentrated suspensions, the diffusion coefficients gradually initially increase from channel centre (zero shear) towards the wall. However, very close to the wall (within two to three particle diameters) the diffusion coefficients decrease strongly, irrespective of particle concentration and flow rate. This indicates that ultimately the wall effect dominates over the shear effect.

Apparent wall slip of colloidal hard sphere suspensions is another important feature in microchannel flows. This kind of slip might be expected due to the depletion of particulate matter near the wall. In that case, the importance of slip should be related to the particle volume fraction of the suspension. This is discussed In **Chapter 5**. Measurements of velocity profiles of different suspensions reveal that the slip velocity (at the wall) grows linearly with shear rate, and more for higher concentration. The apparent slip length, measured as the distance to the wall where the velocity extrapolates to zero, weakly depends on shear rate. But it does show a significant and gradual increase with particle concentration. This experimentally observed dependence on particle volume fraction was described theoretically with a purely geometric argument, combined with an empirical expression for the volume fraction dependent viscosity. This model gives a remarkably good description of our experimental results.

The effect of cylindrical confinement on the structure and diffusive dynamics of colloidal hard sphere has been examined in **Chapter 6**. For this, microcylinders with different radii (2.5 μm to 20 μm) and monodisperse suspensions of various particle volume fractions ($\Phi = 0.05\text{--}0.39$) were prepared. From the measurement of the mean squared displacement (MSD) of colloids inside different cylinders for all concentrations, it is found that the wall effect on particle motion is much more pronounced for dilute suspensions and the effect gradually diminishes with increasing particle concentration. Additionally, we found a clear layering of the particles along the curved interface, and as the cylinder is made smaller the structure gets even more pronounced. Dense systems which form structures, reveal an anti-correlation between the MSDs and the local particle density, most clearly for the particle layer in contact with the wall. MSDs in the azimuthal direction

remain almost independent of the structure. Accordingly, a strong anisotropy in particle dynamics is observed near the wall.

Finally, we believe that our work will open up possibilities to extend the research to more complex geometry and/or colloidal systems, to address some interesting and unsolved fundamental questions. Some interesting ideas are sketched in **Chapter 7**.

Samenvatting

Het in dit proefschrift beschreven werk is gericht op de diffusieve dynamica van colloïden in druk-gedreven stroming in de buurt van een wand, en van colloïden in een stilstaande vloeistof die begrensd zijn door microcilinders. Dit werk behandelt eveneens een methode om in de aanwezigheid van een inhomogeen afschuifveld de diffusiecoëfficiënten te meten. Daarnaast wordt nog onderzocht hoe in een kanaalstroming de schijnbare slip bij de wand afhangt van de dichtheid van de deeltjes in de suspensie.

Het meten van de diffusiecoëfficiënten van colloïden is bijzonder ingewikkeld, vooral in druk-gedreven stroming in microkanalen, omdat de Brownse beweging gesuperponeerd is op de advection. Het is belangrijk om voorafgaand aan het meten van de diffusiecoëfficiënten, de Brownse beweging goed van de advection te ontkoppelen. **Hoofdstuk 3** beschrijft dit probleem en illustreert een nieuwe werkwijze om de intrinsieke stochastische beweging van deeltjes te onderscheiden van ongelijkmatige achtergrondstromingen. Met computersimulaties is bepaald dat deze techniek geldig is voor volumefracties tot $\Phi = 0.4$. De methode gebruikt de ruimtelijke coördinaten van de deeltjes in de tijd als input en meet iteratief de verplaatsing van deeltjes in opeenvolgende tijdsintervallen. Het product van de gemeten snelheid en de tijdstap geeft de verplaatsing en wordt vervolgens van de totale verplaatsing afgetrokken. Op deze wijze wordt de advection uit het snelheidsveld geëlimineerd. Na de laatste iteratie wordt de gemiddelde kwadratische verplaatsing van de colloïden uit de overgebleven afgelegde banen berekend. Deze methode werkt goed voor zowel verdunde als voor geconcentreerde suspensies.

Door afschuiving geïnduceerde diffusie is een op zich niet onbekend verschijnsel. De meeste studies richtten zich tot dusver echter op niet-Brownse deeltjes; ondanks de praktische relevantie werd er weinig gekeken naar colloïden. Het was tot nog toe niet duidelijk hoe het inhomogene afschuifveld de dynamica van colloïden in microkanalen beïnvloedt. In het geval van stromingen in een microkanaal verandert de lokale afschuifsnellheid geleidelijk over de doorsnede van het kanaal, wat invloed heeft op de beweging van de deeltjes en de lokale structuur van de suspensie. De beperkende wanden die nodig zijn om de stroming in stand te houden, hebben ook hun eigen invloed op de dynamica van de deeltjes. In

Hoofdstuk 4 wordt het experimentele bewijs getoond van dat de diffusie van colloïden in de aanwezigheid van afschuiving sterk afhankelijk is van de onderlinge (hydrodynamische) interacties van de deeltjes. Diffusie is onafhankelijk van het lokale Peclet nummer (een dimensieloze afschuifsnelheid) in verdunde suspensies waar de deeltjes nauwelijks interactie hebben. Voor opeengepakte systemen daarentegen (waar sterke onderlinge interactie van de deeltjes heerst), vertonen de diffusiecoëfficiënten van de colloïden een duidelijk transitie van thermische- naar afschuif geïnduceerde diffusie bij een Peclet nummer van ongeveer 1, en nemen de diffusiecoëfficiënten toe bij het groter worden van het Peclet nummer. Deze versterkte diffusie treedt zowel in de richting van de stroming als in de richting van de snelheidsgradiënt op, maar is het meest dominant in de richting van de stroming. Een andere duidelijke observatie is de afname van de diffusiecoëfficiënten in de buurt van wanden ondanks dat de lokale afschuifsnelheid daar maximaal is. Vandaar dat de diffusiecoëfficiënten in dichte suspensies geleidelijk toenemen van het centrum van het kanaal (geen afschuifspanning) richting de wand. Zeer dicht bij de wand (binnen twee tot drie diameters van een deeltje) nemen de diffusiecoëfficiënten echter sterk af, ongeacht de concentratie en de stroomsnelheid van de deeltjes. Dit geeft aan dat uiteindelijk het effect van de wand domineert over het effect van de afschuifspanning.

De schijnbare wandslip van colloïdale harde bollen suspensies is een ander belangrijk kenmerk van microkanaalstroming. Dit soort wandslip kan optreden als gevolg van een lagere deeltjes volumefractie bij de wand. De wijze waarop dit afhangt van de volumefractie, wordt besproken in **Hoofdstuk 5**. Metingen van snelheidsprofielen van verschillende suspensies onthullen dat de slipsnelheid bij de wand lineair toeneemt met de afschuifsnelheid, en groter wordt bij hogere concentraties. De schijnbare wand-sliplengte, gemeten als de afstand tot de wand waar de snelheid naar nul extrapoleert, is licht afhankelijk van de afschuifsnelheid maar vertoont een duidelijke toename met de deeltjesconcentratie. De experimenteel waargenomen relatie tussen de schijnbare wand-sliplengte en de deeltjes volumefractie is theoretisch beschreven met een puur geometrisch argument in combinatie met een empirische uitdrukking voor de volumefractie afhankelijke viscositeit van colloïdale harde bollen. Deze voorspellingen laten een opmerkelijk goede overeenkomst met de experimentele resultaten zien.

Het effect van de cilindrische omhulling op de structuur en de diffusieve dynamica van colloïdale harde bollen zijn behandeld in **Hoofdstuk 6**. Cilinders met

verschillende radii (van 2.5 μm tot 20 μm) en suspensies met verschillende volumefracties ($\Phi = 0.05\text{-}0.39$) zijn onderzocht. Uit de meting van de gemiddelde kwadratische verplaatsing (GKV) van colloïden in de verschillende cilinders en voor de verschillende concentraties is gebleken dat het effect van de omhulling sterker naar voren komt bij verdunde suspensies en geleidelijk afneemt met het toenemen van de deeltjesdichtheid. Dit effect wordt geleidelijk kleiner bij het toenemen van de deeltjesconcentratie. Daarnaast is laagvorming van deeltjes langs de gekromde oppervlakten van de omhulling waargenomen, bij het kleiner maken van de cilinder wordt deze structuur steeds opvallender. Dichte systemen die deze structuren vormen, laten een anti-correlatie zien tussen de GKV's en de lokale deeltjesdichtheid, dit is het meest duidelijk voor lagen van deeltjes die in contact zijn met de wand. De GKV in de azimuthale richting bleef vrijwel onafhankelijk van de structuur. Er is daarom een sterke anisotropie waargenomen in de dynamica van de deeltjes in de buurt van de wand.

Tot slot denken wij dat ons werk diverse mogelijkheden biedt voor vervolgonderzoek met meer complexe geometrie en/of colloïden, om nieuwe fundamentele vraagstukken te kunnen beantwoorden. Een schets van interessante ideeën is weergegeven in **Hoofdstuk 7**.

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Publication list

Publication from this Thesis:

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M.H.G. Duits, S. Ghosh and F. Mugele, 'Measuring advection and diffusion of colloids in shear flow', *Langmuir* 2015, 31, 5689.

S. Ghosh, D. Wijnparle, F. Mugele and M.H.G. Duits, 'Dynamics of Colloids Confined in Microcylinders', *Submitted*.

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'Influence of wall roughness on confined flows', 11th Dutch Soft Matter Meeting, TU Eindhoven, The Netherlands, November 7, 2011.

'Effect of confinement and wall roughness on colloidal suspensions at low Péclet numbers', 13th Dutch Soft Matter Meeting, Wageningen University, The Netherlands, November, 2012.

‘Diffusive behavior of colloidal suspensions flowing through microchannels’, 14th Dutch Soft Matter Meeting, University of Twente, The Netherlands, June 7, 2013.

‘Flow of concentrated suspensions through microchannels’, Flow 14, University of Twente, The Netherlands, May 18, 2014.

‘Effects of shear and walls on the diffusion of colloids in microchannels’, DPG Berlin, Berlin Technical University, Germany, March 16, 2015.

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Poster presentations:

‘Diffusivity in microchannels at low Péclet numbers’, Somnath Ghosh, Dirk van den Ende, Frieder Mugele and M.H.G. Duits, Veldhoven, The Netherlands, 2013.

‘Particle dynamics in dense suspensions flowing through microchannels’, Somnath Ghosh, Frieder Mugele and Michel Duits, Les Houches, France, 2013.

‘Behavior of colloidal suspensions flowing through microchannels’, Somnath Ghosh, Frieder Mugele and Michel Duits, International Soft Matter Conference, University of Rome, Italy, 2013.

‘Self-diffusion of Brownian suspension under shear’, Somnath Ghosh, Frieder Mugele and M.H.G. Duits, FOM 2014, Veldhoven, The Netherlands.

‘Diffusive dynamics of colloids in confined flow’, Somnath Ghosh, Dirk van den Ende, Frieder Mugele and Michel Duits, NWO meeting, The Netherlands, 2014.

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About the author

Somnath Ghosh was born on 5th May, 1984 in India and grew up in a small village named Kamarkita. After finishing his secondary education in 2000, he moved to the nearby city Burdwan for higher secondary education. He later joined Jadavpur University in 2002 for his bachelor degree in Chemical Engineering. He then got a job in Capgemini India Pvt. Ltd. in 2006 and worked there for more than two years. Later he decided to continue his education and got admitted to Indian Institute of Technology, Kharagpur for his master degree program in Chemical Engineering. During this period, he worked with Prof. Dr. Sunando DasGupta. There he experimentally investigated the spreading of thin liquid film under the influence of electric field.

In August 2011, he started his doctoral research under the supervision of Dr. Michael H.G. Duits in Physics of Complex Fluids Group headed by Prof. Dr. Frieder Mugele at the University of Twente. The result of his doctoral research are presented in this thesis.