Accelerated Transport of Particles in Confined Channels with a High Roughness Amplitude

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Supporting Information

ABSTRACT: We investigate the pressure-driven transport of particles 200 or 300 nm in diameter in shallow microfluidic channels ∼1 μm in height with a bottom wall characterized by a high roughness amplitude of ∼100 nm. This study starts with the description of an assay to generate cracks in hydrophilic thin polymer films together with a structural characterization of these corrugations. Microfluidic chips of variable height are then assembled on top of these rough surfaces, and the transport of particles is assessed by measuring the velocity distribution function for a set of pressure drops. We specifically detect anomalous transport properties for rough surfaces. The maximum particle velocity at the centerline of the channel is comparable to that obtained with smooth surfaces, but the average particle velocity increases nonlinearly with the flow rate. We suggest that the change in the boundary condition at the rough wall is not sufficient to account for our data and that the occurrence of contacts between the particle and the surface transports the particle away from the wall and speeds up its motion. We finally draw perspectives for the separation by field-flow fractionation.

INTRODUCTION

The development or improvement of labs on chips dedicated to the separation of molecules or particles has been accompanied by numerous studies focused on particle motion analysis in microfluidic channels.1–3 In the context of confined flows, the consequences of surface–solvent interactions have called for the implementation of specific velocimetry techniques to probe the behavior of particles near solid surfaces.4–7 The transport of particles at the vicinity of hydrophilic or hydrophobic surfaces has been extensively studied with smooth or rough corrugations (see ref 8 for a review). It is commonly accepted that no-slip boundary conditions apply for smooth hydrophilic surfaces.8 Conversely, slip lengths of ∼30 nm can be detected for hydrophobic surfaces,9 and the engineering of textured surfaces with superhydrophobic properties has been performed to reach slip lengths of tens of μm.10,11 For hydrophilic surfaces, the study of particle–particle collisions has shown that the existence of microscopic surface roughness breaks the common assumption that the fluid acts as a lubricant to prevent the solid–surface contacts.12 The occurrence of contacts violates the time-reversibility of Stokes equations for smooth surfaces and Newtonian fluids and leads to a reduction of the effective viscosity of suspensions.13 At the level of individual colloids, the study of transport over surfaces with “smooth” roughness (see, e.g., ref 14), that is, with a corrugation height smaller than the radius of the tracer, indicated that when the contacts occurred, the translational velocity generally decreased, whereas the rotational velocity increased because of the solid–solid friction.

In the field of colloidal transport, many studies have been focused on colloid retention through porous materials. Whenever the roughness size is comparable to or larger than the particle size, particle retention is controlled by water velocity and surface roughness.15,16 Despite its relevance for, for example, geosciences, this regime has been poorly investigated in microfluidic channels. In this report, we therefore set out to investigate the transport of fluorescent nanoparticles of diameter 200 nm in shallow channels 0.5–2.0 μm in thickness with an average maximum peak-to-valley height of ∼100 nm. After the description of a process to generate hydrophilic surfaces with a high roughness amplitude, we monitor the transport of tracers conveyed by pressure-driven flows using wide-field fluorescence microscopy and the nanoparticle velocimetry distribution analysis (NVDA) method.4 We report anomalous transport properties over rough surfaces and discuss their physical origin.

MATERIALS AND METHODS

Rough surfaces were produced through the formation of cracks during the reticulation of a thin layer of 6 μm of “hard” poly-dimethylsiloxane (hPDMS).17 The unreticulated silicone elastomer was spin-coated at 3000 rpm during 30 s on 170 μm glass coverslips. Because of the difference in the thermal expansion coefficient between the polymer film and the substrate, a temperature onset resulted in tensile stresses...
accompanied by the formation of cracks.\textsuperscript{14} We used a slow ramp with a slow baking at 60 °C during 4 h or a rapid one at 80 °C during 45 min. Surface topography characterization was carried out with atomic force microscopy (AFM, Veeco Dimension 3100), optical profilometry (Wyko, Veeco), and scanning electron microscopy (SEM, Hitachi S-4800). Image analysis of the SEM micrographs was carried out in ImageJ using (i) the bandpass fast Fourier transform filter with size thresholds of 250 nm and 15 μm, followed by (ii) the "Find maxima" algorithm with a noise tolerance set to 50 and contour identification, and finally (iii) the “particle analysis” algorithm to infer the perimeter and the surface of each crack pattern (see the Supporting Information Figure S1A).

The channels of microfluidic chips were engraved in silicon wafers using reactive ion etching performed after conventional photolithography, as described in ref 19. The depth of the channel spanned in the range 0.9–1.9 μm. The silicon channels were then sealed to the glass coverslips covered with hPDMS. The bonding step was performed right after surface activation using oxygen plasma (200 W, 30 s). Note that this treatment did not induce detectable contaminants of the crack patterns (Supporting Information Figure S1B) and formed a native silicon oxide layer on the silicon chip. The walls of the resulting chips were transiently hydrophilic, and our experiments were conducted immediately after the bonding step.

Unless stated, chemicals were purchased from Sigma-Aldrich. Fluorescent polystyrene nanoparticles with surface carboxyl groups (Thermo Fisher) were conveyed in the microfluidic chips using a pressure controller operating in the range of 10–500 mbar (microfluidic flow control system, MFCS Fluigent). The viscosity of the fluid was set to \( \eta = 5 \text{ mPa}\cdot\text{s} \) with a 40% (vol/vol) glycerol in water mixture containing the ionic species Tris-HCl (160 mM), boric acid (160 mM), and ethylenediaminetetraacetic acid (5 mM; pH = 8.3). Note that the Debye layer \( \lambda_D \), as defined by the length scale over which mobile charges in the buffer screen out electric fields, was \( \sim 1 \text{ nm} \), which is much less than the surface roughness. The pressure was set to induce a flow maximum velocity typically slower than 300 μm/s, implying that the flow and particle Reynolds numbers were \( 10^{-4} \) or less. The transport of nanoparticles was assayed by tracking them with a wide-field Zeiss fluorescence microscope equipped with a 100× objective (numerical aperture = 1.3) and a Zyla SCMO camera with a pixel size of 160 nm. The fluorescent particles of diameter 2a = 200 or 300 nm were diluted at a typical (v/v) ratio of 1:5000 to neglect the interparticle hydrodynamic interactions and to ensure independent tracking. The focal depth of the objective of \( 1.5 \mu m \) was comparable to the channel height, so tracers remained in focus throughout their migration across the field of view of the microscope. Under each experimental condition, 30–50 particle trajectories with a total of \( \sim 5000–8000 \) positions were recorded to extract the velocity distribution along and transverse to the flow direction in the field of view of the microscope.

### RESULTS

**hPDMS Surface Roughness Characterization.** Smooth hPDMS thin films were obtained with a baking process at low temperature, whereas crack patterns were systematically detected using sharper temperature ramps during the reticulation of hPDMS (Figure 1A–C). These cracks had a lateral extension of a few microns, and their vertical topography showed corrugations of a maximal height of \( \sim 80 \text{ nm} \), as inferred from AFM (Figure 1D). Note that these cracks were superficial because their depth was much smaller than the thickness of hPDMS films of 6 μm. We then focused on the perimeter–area relationship of the crack patterns based on the analysis of AFM and SEM images (Figure 1E, see Methods in the Supporting Information Figure S1). The resulting graph showed a constant power-law response over three decades associated to an exponent of \( \sim 0.7 \). For simple Euclidean patterns, the perimeter is expected to scale with the square root of the area, that is, the exponent is 0.5. More complex shapes with fractal characteristics are instead characterized by higher
exponents, confirming earlier observations that the formation of cracks in thin films is associated to fractal geometries.

Next, we assayed the roughness parameters of the surface, as inferred from the root mean square average and the average peak-to-valley height, which are denoted as \( R_a \) and \( R_p \), respectively. For flat surfaces, the roughness parameters \( (R_a, R_p) \) were \((1, 11)\) and \((2, 20)\) nm according to AFM and optical interferometry over the scanning areas of \(25 \times 25\) and \(100 \times 100\) \(\mu\)m\(^2\), respectively. Enhanced roughness parameters of \((15, 193)\) and \((18, 100)\) nm, respectively, were detected after the baking process at a high temperature. Our measurements, therefore, demonstrate that hPDMS surfaces with roughness amplitude and fractal topology can be generated using a sharp temperature gradient during the baking process.

**Particle Velocimetry over Smooth hPDMS Surfaces.** We fabricated silicon chips of height \(2h = 930 \pm 15\) nm, as inferred from mechanical profilometry (not shown), with a smooth hPDMS bottom wall (Figure 2A). We investigated the transport of Brownian particles of diameter \(2a = 200\) nm for a set of pressure drops (see the Supporting Information Video) and analyzed it with the NVDA model. The breadth of the transverse velocity distribution was dictated by thermal fluctuations, and it was fitted with the same Gaussian function for every pressure drop to determine the particle diffusion coefficient (data not shown). The longitudinal velocity distribution was instead increasingly skewed as the pressure drop increased (colored datasets in Figure 2B). This distribution resulted from the convolution of the parabolic fluid velocity profile with thermal fluctuations. Qualitatively, the peak of the distribution corresponds to the maximum flow velocity \(v_0\), and the minimal velocity occurs for particles traveling at the vicinity of the walls at \(\sim 2v_0/\mu\)m/h. We showed that the longitudinal distribution could be fitted with a numerical function calculated with hydrodynamic first principles. This function was defined by two parameters, namely, \(v_0\) and the confinement ratio \(a/h\), which could be determined with precisions of 1 and 8\%, respectively, as inferred from simulations and experiments in glass microchannels 2 \(\mu\)m in height.

By setting the confinement ratio to 0.21, we could fit the longitudinal velocity distributions on the smooth hPDMS surfaces using the maximum flow velocity as an adjustable parameter (line plots in Figure 2B). The variation of \(v_0\) as a function of the pressure drop showed a linear response expected for Newtonian fluids (Figure 2C). Furthermore, the slope of \(h^2/2\eta\) allowed us to independently estimate the channel height. Its value of \(2.3 \times 10^{-11} \text{ m}^2/\text{Pa s}\) corresponded to \(2h = 960\) nm, given the viscosity of \(\eta=5\) mPa-s. This estimate was, therefore, in good agreement with our calibration of \(2h = 930 \pm 15\) nm by mechanical profilometry. Consequently, the particle transport in the smooth hPDMS chips was consistent with the behavior observed on the flat glass surfaces. Notably, this result was consistent with the consensus view that the slippage is negligible even at the nm scale on hydrophilic surfaces.

**Particle Velocimetry over Surfaces with a High Roughness Amplitude.** Next, we carried out the same experiment in microfluidic chips of height \(h = 1.2\) \(\mu\)m with a rough bottom wall. We extracted the longitudinal velocity distribution for a range of pressure drop of \(10-100\) bar/m (colored datasets in Figure 3A). We set the confinement ratio to 0.17 and attempted to fit these data with NVDA, with the maximum velocity \(v_0\) as an adjustable parameter. In contrast to the smooth hPDMS surfaces, the distributions were not reproduced because the proportion of low-velocity states, which is zoomed in on the plot in Figure 3B, was much lower than the prediction of the model. We also investigated the particle transport with a set of microfluidic chips of height 0.95, 1.4, and 1.9 \(\mu\)m. In every setting, we detected that the velocity distribution had an anomalous shape in comparison to the canonical response recorded over the flat surfaces (Supporting Information Figure S2A).

Finally, we investigated the response of two different types of tracers of 200 and 300 nm simultaneously flowing, that is, traveling at the same flow rate, in a channel of height 1.6 \(\mu\)m. The different types of particles were segmented based on their difference in the intensity of \(\sim 3\) fold to extract their respective velocity distributions (histograms in Figure 3C). We noted that
the velocity distribution for the 300 nm particles was slightly more skewed toward high velocities than that obtained with 200 nm beads. Both distributions were also shifted for the low-velocity states in comparison to the canonical response over flat walls (black curve, Figure 3C).

**Analysis of the Maximum and Average Velocity with a Rough Surface.** Because we have no model to fit the velocity distribution with rough walls, we wished to characterize the anomalous shape of the velocity distribution based on the average and maximal particle velocity, as inferred from the first raw moment and the position of the peak of the distribution. We plotted the variation of the maximum velocity as a function of the pressure drop (blue data set in Figure 4A) and observed a linear trend with a slope of \(3.35 \times 10^{-11} \text{m}^2/\text{Pa} \cdot \text{s}\) (solid black line in Figure 4A). Assuming flat surfaces, the measure of the slope could be used to estimate the channel height of \(h = 1.24 \mu\text{m}\). This measurement was in good agreement with our characterization of silicon chips by mechanical profilometry. Interestingly, this result was consistent with the observation that surface roughness had a minor effect on the hydraulic resistance in the laminar regime.\(^{24}\)

Next, we focused on the variation of the average velocity as a function of the pressure drop (green data set in Figure 4A). We expected the average velocity to be equal to \(2/3\) of the maximal velocity because of the slit-like geometry of our channels, as indicated by the dashed line in Figure 4A. Yet, we observed that the average velocity tended to increase nonlinearly with the pressure drop with a power law exponent of 1.2 (green line in Figure 4A). This effect is a consequence of the changes of the velocity distribution function shown in Figure 3A,B associated to the reduction in the low-velocity states. Noticeably, the linear and power-law responses for the particle maximum velocity and average velocity, respectively, were detected for the different levels of confinement (Supporting Information Figure S2).

**DISCUSSION**

Because alterations of the boundary conditions at the walls would change the density of the low-velocity states, we tested whether the slippage could account for our data.\(^9\) Notably, effective slip lengths have been theoretically and numerically studied for laminar flows over rough surfaces.\(^{25,26}\) Qualitatively, the up-and-down motion of the particle induces a mean slip velocity associated to an apparent translation in the bulk of the...
Using finite element simulation of 2D flows in a channel of 1.2 μm in height (Supporting Information Figure S3), we measured the flow velocity at a distance of 100 nm of the wall, that is, for the particles contacting the tip of the corrugations and noticed an acceleration to an apparent slip length of ~20 nm, and to investigate this effect further, we fitted the velocity distributions with the NVDA model including a slip velocity at the wall (see the Supporting Information). Note that the particle diameter was set to 200 nm and the channel height to that deduced from our calibration by profilometry (see the legend of Figure 4B). The slip velocity was plotted as a function of the shear rate at the wall for every set of data collected with the rough hPDMS surfaces (colored data points in Figure 4B). The graph was qualitatively fitted with a line, the slope of which defined a slip length of ~100 nm. This value was about 5 times greater than our qualitative estimate, suggesting that the apparent slip could not account alone for our results.

In another nonmutually exclusive direction, we suggest that the anomalous transport properties may be related to the occurrence of surface–particle contacts. Using millimeter-scale flow cells with a rough surface obtained by the adsorption of a monolayer of millimeter-scale particles, it has indeed been shown that the longitudinal velocity of the particles traveling at the vicinity of the wall increased nonlinearly with the shear rate of the flow.27 This study proposed that the acceleration in the particle motion was because of the transfer of momentum through interactions with the asperities of the surface and the subsequent flight over the surface. This mechanism is slightly analogous with the combination of rolling and slipping undergone by colloids brought into contact. Note that such contacts break the fore-and-aft symmetry of the trajectories predicted for smooth spheres conveyed in a viscous fluid.12,28 The occurrence of particle–surface contacts associated to the roughness of the hPDMS layer could therefore lead to an apparent depletion of the low-velocity states in the particle velocity distribution and therefore account for our data.

**CONCLUSIONS**

Altogether, we present a technology to fabricate shallow channels with a bottom wall with a high roughness amplitude, which is composed of cracks with a fractal geometry. We then analyze the transport of particles in these microfluidic systems with the NVDA method. We analyze the particle velocity distribution and demonstrate that its profile is consistent with a Poiseuille flow with smooth hPDMS surfaces but departs from this “canonical” response with rough surfaces. On the basis of the analysis of the maximum and average particle velocity, we conclude that the slippage is unlikely to account for our results and suggest that particle–surface contacts and the associated transfer of momentum are potential explanations. This mechanism of particle–surface transfer momentum has not been thoroughly documented in microfluidic systems, but several studies have been focused on colloid retention through porous materials with a high roughness amplitude for groundwater contamination. Microfluidic technologies offer ideal solutions to build model “rock-on-a-chip” systems29 dedicated to the characterization of confined transport and surface “trapping” with rough walls. Notably, surface trapping should be studied with the same chemistry and roughness parameters for the upper and lower walls of the channels to obtain results qualitatively comparable to those in porous materials. In another mutually reinforcing direction, we suggest that the measurement of the average velocity of the particles traveling in confined channels may find an unexpected application for minimally invasive monitoring of microsystem aging, if mechanical constraints induce the formation of cracks.

Our results also raise perspectives for separation science because the degree of roughness of a shallow channel may provide a control parameter to enhance field-flow fractionation (FFF) technologies.3 A standard mode of transport for FFF separation combines transverse forces toward the channel walls together with longitudinal advection. The colloids then travel at the vicinity of surfaces, which are usually assumed to be smooth. We thus hypothesize that colloid migration could be finely tuned by tailoring the geometry and distribution of asperities to selectively immobilize (and hence sort) particles. These research studies should be associated to fluid flow modeling at smaller length scales because molecular dynamics simulations have uncovered complex fluid structures at the vicinity of rough walls with fractal geometries.10–32 The resulting data may shed light on the molecular origin of transverse forces away from the walls, which have been detected by FFF,33,34 the physical origin of which remains controversial.35

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b03962.

Particles (200 nm) traveling over a rough hPDMS surface; model of transport in the presence of slippage at the walls; structural characterization of crack patterns by image analysis of SEM; NVDA analysis of 200 nm particles traveling in rough channels of 900, 1400, and 1950 nm in height; 2D COMSOL simulations of Poiseuille flows over rough surfaces; and estimation of the apparent slip length for 200 nm particles (PDF) Transport of Brownian particles (AVI) (PDF) (AVI)

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**Notes**

The authors declare no competing financial interest.

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