Analysis of wall effect on the process of diffusion of nanoparticles in a microchannel

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Abstract. In this preliminary work we introduce a new method for verification of the no-slip boundary condition on the liquid-solid interface, by analyzing variations in Brownian motion coefficients of colloidal nanoparticles as a function of distance from the wall. The experimental investigations are performed in a small channel using an epi-fluorescent microscope. For precise measurements close to the wall an evanescent wave illumination is used. The experimental data obtained for 300nm particles gave us evidence of relatively large (0.3µm) slip length. The experiments are supplemented by two-dimensional Molecular Dynamics simulations.

1. Introduction
Recently, the classical no-slip hypothesis for the tangential velocity of liquid adjacent to the solid surface became questioned for the flow in micro- and nanofluidic devices. The topic is of fundamental interest and has potential practical consequences in many areas of applied sciences. For small-scale geometries this slip can be significant permitting for nearly frictionless flow in 2nm carbon nanotubes [1].

Hence, several experimental and numerical studies has been performed to demonstrate and explain presence of the molecular-scale slip at the fluid-solid interface (see the reviews by Neto et al. [2], Lauga et al. [3]). The key factor is that the continuum fluid dynamics still holds within the interior of the liquid and the slip is due entirely to discontinuity in speed between the wall and adjacent liquid layer. Molecular Dynamics simulations [4] gave some insight into the problem, suggesting localized hoping of adjacent to the wall liquid molecules or discontinuous motion of the whole molecular layers.

Slip is usually viewed from the averaged flow properties over all liquid molecules near the solid boundary and expressed as slip length, which is determined by extrapolating velocity profile beyond the channel wall (Fig. 1).

The amount of the slip is quantified in terms of the shear rate and local flow velocity using following formula:
\[ U_s = \lambda \dot{\gamma}, \]
\[ \dot{\gamma} = \frac{dU(z)}{dz}, \]

(1)

where:
- \( U \) - fluid velocity,
- \( U_s \) - fluid velocity at the wall,
- \( \dot{\gamma} \) - shear rate,
- \( \lambda \) - slip length.

From the theoretical point of view (Molecular Dynamics studies [4]) the slip length strongly depends on the shear rate and varies from fractions of nanometer to few nanometers only. Experimental studies indicate much larger slip variation, covering range from several nanometers to several micrometers (see collection of data by Lauga et al. [3]). This ambiguity is mainly due to different surface treatments and different liquid/solid interactions like wetting - non-wetting. But perhaps the main source of differences comes from experimental difficulties in performing accurate velocity measurements of the flow at molecular distances from the wall [8, 9, 10, 11, 12].

![Figure 1. Navier slip law.](image)

To avoid problems appearing in reconstructing flow velocity profile in nanometric liquid layers, we propose to evaluate how the slip/no-slip boundary conditions affect behavior of a Brownian particle performing its chaotic motion close to the wall. In physics Brownian motion has been a continuous inspiration for understanding diverse transport processes. It was found that depending on fluid properties, molecular size ratio [5], or spatial constrains [6, 7] stochastic motion of Brownian particle changes. By evaluating deviations of the diffusion coefficient one obtains a micro-scale sensor of local liquid parameters and flow conditions.

In the fluid bulk, the diffusivity \( D \) of an isolated particle follows the Stokes-Einstein relation, which balance the fluid thermal energy with the particles hydrodynamic mobility. In the vicinity of the wall hydrodynamic mobility changes and depends on the direction of the particle motion. The diffusion coefficients \( (D_\perp, D_\parallel) \) for a single particle close to the wall can be defined by the following expressions:

\[ D_\perp = \beta_\perp D, \]
\[ D_\parallel = \beta_\parallel D, \]

(2)

\[ D = \frac{k_B T}{3\pi \mu d_p} \]

(3)
where:
\( D_{\perp} \) - diffusion coefficient towards the wall,
\( D_{\parallel} \) - diffusion coefficient parallel to the wall,
\( \beta_{\perp} \) - perpendicular variation,
\( \beta_{\parallel} \) - parallel variation,
\( D \) - bulk diffusion coefficient,
\( k_B \) - boltzman constant,
\( T \) - temperature,
\( \mu \) - viscosity,
\( d_p \) - particle diameter.

The hydrodynamic mobility of the particle close to the wall depends on the boundary conditions imposed for the velocity field at the wall. The slip or no-slip boundary conditions change apparent diffusivity of the particle. Lauga and Squires \[13\] evaluated this effect by deriving general formula for the diffusion coefficient of a single particle as a function of the distance \( h \) from the wall, and the slip length \( \lambda \) assumed for the kinematic boundary conditions:

\[
\beta_{\perp} = 1 - \frac{3d_p}{8h} [1 + 2I(Kn)] + O \left( \frac{d_p^3}{8h^3} \right),
\]

\[
\beta_{\parallel} = 1 + \frac{3d_p}{16h} [1 - 2J(Kn)] + O \left( \frac{d_p^3}{8h^3} \right),
\]

where: \( h \) - is distance from particle center to the wall. Knudsen number \( Kn = \lambda/h \) represents nondimensional measure of the slip length.

Functions \( I \) and \( J \) are defined by the following integrals \[13\]:

\[
I(Kn) = \int_0^\infty \frac{x^2}{1 + 2xKn} e^{-2x} dx,
\]

\[
J(Kn) = \int_0^\infty \frac{(1 + xKn)(1 - x)^2 + 2(1 + 2xKn)}{(1 + xKn)(1 + 2xKn)} e^{-2x} dx.
\]

Here, the above formulation is used to evaluate effect of the wall on the Brownian motion of nanoparticles suspended in water. The same procedure is used for the data obtained from the numerical simulations using Molecular Dynamics and for the experimental study. Having distance \( h \) of the analyzed particles from the wall and their diffusion coefficients \( \beta_{\perp}, \beta_{\parallel} \), by inverting the \( I \) and \( J \) integrals we may evaluate the Knudsen number \( Kn \), hence the slip length \( \lambda \) for parallel and perpendicular to the wall flow velocity components. In this way the slip length as a function of distance from the wall \( h \) is obtained.

Figure 2 shows variation of \( I \) and \( J \) functions with Knudsen number \( Kn \). It can be noticed that the main effect of the slip length can be found for \( Kn \) in the range of 0.1 to 10. In this range a relatively small change of \( Kn \) results with a quite strong variation of both functions involved in the correction of the diffusivity constant. The largest effect can be expected for parallel component of the diffusion constant \( \beta_{\parallel} \) variation.

2. Simulations

The Brownian diffusion of 24 nm carbon nanoparticle suspended in water in an infinite channel formed between two quartz walls (Fig. 3) was simulated by the molecular dynamics code LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator). The computations were performed for the square domain of 310.5 nm size and periodic boundary
Figure 2. Variation with the Knudsen number $Kn$ of the functions $I$ and $J$ involved in the correction to perpendicular and parallel diffusivity close to the wall.

conditions for the two side walls. All interactions between particles were described by the Lennard-Jones potential:

$$U(r) = 4\epsilon \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}$$  \quad (6)

where:

- $\epsilon$ - potential well depth,
- $\sigma$ - distance at which the potential is zero,
- $r$ - distance between molecules.

The colloidal particles as well as the walls were defined as independent rigid bodies. This means that at each time step the total force on each rigid body is computed as the sum of the forces on its constituent particles and the coordinates and velocities of the atoms in each body are updated so that the body moves and rotates as a single entity. The following potential parameters where used for all simulations:

$$\epsilon_{H_2O} = 0.155 \frac{\text{kal}}{\text{mol}}, \sigma_{H_2O} = 3.1536 \AA - \text{liquid particles},$$

$$\epsilon_C = 0.102 \frac{\text{kal}}{\text{mol}}, \sigma_C = 3.35 \AA - \text{colloid particles},$$

$$\epsilon_{SiO_2} = 0.9882 \frac{\text{kal}}{\text{mol}}, \sigma_{SiO_2} = 2.503 \AA - \text{wall particles}.$$
For calculating the parameter of interactions between different types of particles (i and j) the Lorentz-Berthelot mixing rules were used:

$$
\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2},
$$

$$
\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}.
$$

The cut off distance was set to $3\sigma$. The time step was set to $0.1\,fs$ and the number of time steps was $2 \times 10^6$. In each simulation the number of particles was nearly $10^6$. Data was gathered after the simulation reached equilibrium state, which was after about $5 \times 10^5$ time steps. A standard Velocity-Verlet integrator was used to calculate forces.

To calculate the diffusion coefficient the following formula was used:

$$
D = \frac{<s^2>}{A\Delta t},
$$

where:

- $\Delta t$ - time,
- $s$ - distance,
- $A$ - dimension coefficient, equals 2, 4, or 6 for 1D, 2D and 3D problem.

Several simulations were performed to evaluate Brownian motion of colloidal particles placed close to the wall. By calculating the parallel displacement and by knowing the particle distance from the wall we could estimate the average slip length which is given by (5):

$$
\beta_\parallel = 0.52, \ h = 12.3nm \ \lambda = 3.25nm
$$

The outcome of this preliminary numerical analysis suggests relatively small slip length. Generally, it is in accordance with Molecular Dynamics simulations reported for the channel.
However, due to the obvious constrains of our numerical model (short physical simulation time, two-dimensional domain, frozen wall molecules) the obtained value needs further verification. Additional long time simulations with particles placed at different distances from the wall are continued.

3. Experiment

In the experimental study we analyzed the Brownian motion of fluorescent particles with a diameter of 300 nm suspended in water kept between two quartz walls of a microchannel. The distance between the lower and upper wall of the channel was 500 µm. To obtain precise measurements very close to the upper wall evanescent wave was generated by total internal reflection of the illuminating laser beam (Fig. 4). Light undergoes total internal reflection (TIR) at a refractive index interface between a dense medium with high refractive index (glass) and a less dense medium (water) when the angle of incidence $\alpha$ exceeds the critical value. Then part of the light penetrates into the less dense medium and propagates parallel to the interface with an intensity that decays exponentially with the normal distance from the interface. This evanescent wave illumination has been used extensively in the life sciences. Recently it was rediscovered in microfluidics for near wall flow measurements [3]. The main advantage of the method is possibility to reduce the depth of focus of the system below 100 nm. Hence, we use TIR method to obtain images only of particles which are in the vicinity of the wall. All other particles suspended in the liquid stay out of the illuminating sheet and are practically invisible for the acquisition system.

**Figure 4.** Graphical representation of evanescent wave illumination.

The cavity formed between two quartz plates once filled with water suspension of fluorescent particles was sealed and mounted on the microscope table. A quartz prism was attached to the upper wall to couple the laser light beam into the channel. The penetration depth is a function of incidence beam angle on the prism as it is illustrated on Figure 5. A precise mechanical system equipped with movable mirrors was used to set appropriate incidence angle. Having fixed light incidence angle the penetration depth in the setup could be calculated using the following equations:

$$d = \frac{\Lambda}{4\pi \left[ \eta_1^2 \sin^2 \left( \frac{\pi}{4} + \arcsin \left( \frac{\sin(\alpha)}{\eta_1} \right) \right) - \eta_2^2 \right]^{-\frac{1}{2}}}$$

(10)

where:

- $\alpha$ - angle of the incident beam,
- $\eta_1, \eta_2$ - refractive index of glass and water,
- $\Lambda$ - laser wavelength.
Figure 5. Penetration depth as a function of light incidence angle.

Figure 6. Microchannel under the microscope. Total internal reflections of the laser in the upper wall can be seen.

Fine adjustment of the laser illumination angle allowed us for a precise control of the penetration depth of the evanescent wave, which was set to be $d = 107 \pm 6\text{nm}$. This way only the particles within the penetration depth where illuminated strongly enough to be detected by the camera. The measurements were performed under an epi-fluorescent microscope (Nikon Eclipse 50i), for particles located in the $107\text{nm}$ light sheet close to the wall and in the centre plane of the channel height (Fig. 6). Microscopic images were acquired using a high speed camera (PCO1200HS). The evanescent wave illumination was formed using $1kHz$ Nd:YAG pulsed laser (Ekspla NL202/SH/TH) with $532\text{nm}$ light wavelength. The temporary
positions of the particles were evaluated from the long sequences of acquired microscopic images by means of especially developed filtration and image analysis MATLAB codes. Each sequence consists of 650 images. In order to reduce static noise, a mean image of a sequence was calculated and then subtracted from each frame. This way only moving particles were clearly visible. To find the exact positions of the particles, each point of a frame was correlated with a theoretical model of a particle image. Places where the correlation value was above 0.6 particle position was found. Since light intensity of a particle image has a two dimensional Gaussian profile, the theoretical model image (Fig. 7) is given by the following equation:

$$f(x, y) = \exp\left(-\frac{x^2 + y^2}{2\sigma^2}\right).$$

(11)

Figures 8 and 9 show a typical image before and after the applied filtration. In the second image one may easily observe detected particles encircled for better visibility.

Once all of the images were analyzed, the identified particles were used to build individual particle trajectories. The concentration of particles was set so that the maximal displacement of a single particle between frames is much smaller than the mean distance between other particles. That way the algorithm for finding trajectories won’t mix the particles and we minimize the possibility of producing false displacements.

Images where calibrated using a precise optical scale. For the lens of magnification 20x the pixel square size was 0.6µm, and for the objective of magnification 60x the size was 0.25µm. Figure 11 shows a typical trajectory of one of the particles. The evanescent wave illumination used had penetration depth of 107nm and for 300nm particles only those which center was closer than about 200nm from the wall could be visualized. With decreasing distance from the wall their images became brighter and larger. Precise evaluation of the size of particle spots on the images allowed us to find their apparent diameter, hence to evaluate their distance from the wall. The average distance of a particle center from the wall was found this way to be about $h = 170nm$.

The diffusion coefficient was calculated in the same manner as in the numerical simulation using equation (9). Since we only observe particle movement in the plane parallel to the channel wall, only the parallel diffusion coefficient can be obtained from the present experiment. Two sets of measurements were performed. Measurements far from the wall were performed by observing particles in the middle of the channel and illuminating them by a fluorescent lamp of the microscope. Measurements close to the wall were done using evanescent wave illumination. From the measurements performed in the middle of the microchannel height we obtained the diffusion constant in the bulk of the fluid. By doing measurements close to the wall we obtained the parallel diffusion constant for particles close
**Figure 8.** Image of particles close to the wall with a lot of static noise before filtration.

**Figure 9.** The same image after filtration and noise reduction, with only moving particles localized.

**Figure 10.** Typical trajectory of a Brownian motion. The particle was 300 nm in diameter, time between points is 0.5 s.
Table 1. Diffusion coefficients measured in the cavity centre and close to the wall.

| Measurement | In the bulk | | Near the wall | | |
|-------------|-------------|-------------|-------------|-------------|-------------|
| I           | 1.49        | I           | 0.79        | | |
| II          | 1.30        | II          | 0.83        | | |
| III         | 1.10        | III         | 0.84        | | |
| IV          | 1.33        | IV          | 0.82        | | |
| V           | 1.19        | V           | 0.92        | | |
| mean        | 1.28        | mean        | 0.84        | | |

Figures 11 and 12 illustrate displacements for 300nm particles close to the wall measured in two perpendicular direction, both parallel to the wall. These two displacement components were used to evaluate the diffusion constant.

By calculating the mean diffusion coefficient and by knowing the particle distance form the wall we can estimate the slip length using formulations given by (5). Based on these measurements near wall diffusion coefficient is $\beta = 0.66$. For the average particle distance from the wall $h = 170nm$ the evaluated slip length is given as $\lambda = 300nm$.

This relatively large value still remains within spread of data reported in the literature ($5nm - 10\mu m$). Usually large slip length is associated with superhydrophobic surface properties or high surface roughness. In our case measured average roughness of the quartz glass used was below 1nm. Detailed study of the wall surface under AFM microscope excluded presence of gas pockets or nano-bubbles, which are often reported as slip triggering agents [3]. Also the measured wetting angle for the glass wall was in average equal 40° discarding effects of strong hydrophobic wall properties.
4. Conclusions
Our preliminary numerical simulations suggest absence or very small slip effect for the Brownian motion of nanoparticles. It is generally in agreement with reported MD simulations for the slip length found for shear flow in a microchannel. It was shown that substantial slip develops in nonwetting situations when the contact angle is larger than $90^\circ$, with slip lengths reaching 10 - 50 molecular sizes [12]. Nevertheless, it must be concluded that molecular simulations of Brownian motion performed for short time scales and constrained by dimensions of several hundreds nanometers may not properly represent long time self diffusion coefficient of the particle. This work is still in progress. Additional numerical test are necessary to elucidate how far the slip length obtained for Brownian motion relates to that calculated for shear flow.

Our preliminary experimental data for the slip length indicates relatively large value of about $0.3\mu m$. This value is quite large not only in contrast to the simulations but also compared with several experiments performed for hydrophilic surfaces. This may be due to the relatively large particles used, comparable to the distance from the wall and to the penetration depth of the evanescent wave. Since the camera used has a large noise, it was impossible to determine the exact particle distance $h$ from the wall based on the particle image size and its intensity. The work is continued using smaller particles (24nm) and using a new intensified camera. We will be also taking into account modification of the wall properties to verify effect of hydrophobic and hydrophilic interactions.

References
[1] Holt J K, Park H G, Wang Y, Stadermann M, Artyukhin A B, Grigoropoulos C P, Noy A, Bakajin O 2006 Science 312, 1034-1037
[2] Neto C, Evans D R, Bonaccurso E, Butt H-J, Craig V S J 2005 Rep. Prog. Phys. 68, 2859-2897
[3] Lauga E, Brenner M P, Stone H A 2007 In Handbook of Experimental Fluid Dynamics (ed. J. Foss, C. Tropea, A. Yarin), chap. 17, 1219-1240, Springer
[4] Martini A, Roxin A, Snurr R Q, Wang Q, Lichter S 2008 J. Fluid Mech. 600, 257-269
[5] Kalwarczyk T, Zieebacz N, Bielejewska A, Zaboklicka E, Koynov K, Szymanski J, Wilk A, Patkowski A, Gapisinski J, Butt H-J, Holyst R 2011 NanoLetters11, 2157-2163
[6] Fakhri N, MacKintosh F C, Lounis B, Cognet L, Pasquali M 2010 Science 330, 1804-1807
[7] Franosch T, Grimm M, Belushkin M, Mor F, Foffi G, Forro L, Jeney S 2011 Nature 478, 83-88
[8] Lumma D, Best A, Gans a, Feuillebois F, Radler J O, Vinogradova O I 2003 Physical Review E 67, 056313
[9] Tretiweay D C, Meinhart C D 2002 Phys. Fluids 14, L9-L12
[10] Tretiweay D C, Meinhart C D 2004 Phys. Fluids 16, 1509-1515
[11] Joseph P, Tabeling P 2005 Phys. Rev. E 71, 053003
[12] Cottin-Bizonne C, Cross B, Steinberger A, Charlaix E 2005 Phys. Rev. Lett. 94, 056102
[13] Lauga E, Squires T M 2005 Phys. Fluids 17, 103102