Constrained Brownian Motion of a Single Ellipsoid in a Narrow Channel

Han-Hai Li1,2, Zhong-Yu Zheng1,2, Yu-Ren Wang1,2,*

1National Microgravity Laboratory, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190
2School of Engineering Sciences, University of Chinese Academy of Sciences, Beijing 100049

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We study the Brownian motion of a single ellipsoidal particle diffusing in a narrow channel by video-microscopy measurement. The experiments allow us to obtain the trajectories of ellipsoids and measure the diffusion coefficients. It is found that the channel constraints lead to suppression of the particle motion, especially the perpendicular motion to the channel, and the long axis of the particle tends to be parallel to the channel. A stable stratification phenomenon is observed, which is rarely discussed in studies of spherical particles. We also derive an approximate solution of theoretical prediction with the method of reflections, and obtain numerical simulation results using finite element software. They are proven to be effective by comparing them with the experimental results. All of these indicate that the aspect ratio and size of ellipsoid, the width of channel, and the transverse position distinctly affect the Brownian motion of ellipsoids.

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In many biological and industrial processes, such as cell transport,[1] drug transport[2] and microfluidic control,[3] many problems of single-particle diffusion in one-dimensional (1D) narrow channels are encountered. The diffusion behavior of a single Brownian particle has been intensively studied in the infinite 3D space[4] and quasi-two-dimensional (q2D) constraint. However, few works have been carried out under the quasi-one-dimensional (q1D) constraint. Unlike the 3D unbounded case, the main difficulty in studying q1D and q2D problems is that the wall-drag effect dramatically affects the diffusive behavior of Brownian particles. The wall-drag effect arising from the nonzero size of a particle and the flow field must satisfy the boundary conditions imposed by the geometric confinement. In these problems, in addition to the shape of particles, we also need to consider the relative size of particles to the geometric confinement and the relative position of particles. In practice, non-spherical particles diffusing in confined geometries are widespread, such as colloidal ellipsoids,[5,8] bacteria,[6] carbon nanotubes,[9] rigid fibers[10] and molecules[11] To date, few quantitative measurements of diffusion of anisotropic particles in q1D have been reported.

In this letter, we report the results of how q1D confinement affects the translational and rotational self-diffusion of a single ellipsoidal particle. We note that the effects are related to three factors: the shape of the particle, the relative size, and the relative position of the particle in the channel. Thus six (1−7.5) different aspect ratios (p) and three widths (4, 5 and 6 µm) (w)—in total 18 samples—were used in our experiments. Lastly, the theoretical predictions by the method of reflections and the results of finite element simulations are reported and quantitatively compared with the experimental results.

Polystyrene ellipsoids were fabricated by stretching and 3.26 µm diameter polystyrene spheres (Spherotech Inc) with the method described in Refs.[6,13]. Briefly, we placed 1% by weight spheres into a 1% by weight aqueous polyvinyl alcohol (PVA) solution residing in a Petri dish. After water evaporation, the PVA film was stretched at 130°C. The polystyrene spheres embedded in the film are readily stretched under these circumstances since their glass transition temperatures are below 130°C. After cooling to room temperature, the PVA was dissolved and ellipsoids were obtained. To study the effect of the particle shape (p) on the diffusion behavior, we prepared colloidal ellipsoids with five different aspect ratios p = a/b = 1.8, 2.2, 2.8, 5.2 and 7.5, where a and b are the semi-major and semi-minor axes of the ellipsoid, and they were measured by optical microscopy.

The experiments were conducted using microfluidic lab-on-a-chip devices. The polydimethylsiloxane (PDMS) channels were molded from a photomask pattern on a silicon wafer by soft lithography, with 4, 5 and 6 µm widths (w) and 5 µm depth (h) to expound the effect of the geometry of the confinement.

A drop of the suspension was confined in the PDMS mold substrate surrounded with ~100-µm-thick paraffin, and sealed with a microscope cover slip by UV sensitive glue, thus the top of the groove was open to a layer of fluid, and the upper sides of the channels were open. Particle movements were observed by fluorescent microscopy (Nikon A1R) under 40x objective, and recorded by a charge-coupled device camera at 10 frames per second to obtain time-dependent trajectories of the particles (Fig.1). The center positions and orientations of individual ellipsoids in each video frame were tracked using our image-processing algorithm in interactive data language with 0.07 (0.04) µm long (short) axial resolution and 1° angular resolution.[6,8] The vertical separation (h′ in Fig. 4) between particles and the bottom of the groove was determined (~2.4 µm) by measuring

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**Corresponding author. Email: yurenwang@imech.ac.cn

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the diffusion coefficient of isolated reference ellipsoids, which were in the same focal plane as the ones in the grooves, using the method described in Refs. [5, 14].

Depending on the transverse separations \((y)\) between the particles and the center of the channel, we formed three statistical intervals at \(y/w = 0, 0.1\) and 0.2, respectively (see Fig. 1). Based on the observed particles’ \(y\) distribution at \(t = 0, 50\) and 100 s for \(p = 1.8, 2.8\) and 7.5 (see Fig. 2), we found that the transverse relative positions between the particles and the center of the channel changed marginally with time, indicating that the extent of ellipsoid displacement transverse to the channel \((y\)-direction) is very small, and there was a restricted motion in the \(y\)-direction owing to the strong \(y\)-direction confinement. These findings reveal the extreme suppression of the transverse motion of ellipsoidal particles due to hydrodynamic interactions by the channel-like confinement. The consequence is that the ellipsoidal particles in our experiment exhibit q1D motion. Therefore in this study, we henceforth focus on the motion along the channel \((x\)-direction).

We measured the translational diffusion coefficients \((D^T)\) of ellipsoids at three different transverse positions, defined as \(D^T(y/w) = \frac{\langle (\Delta x)^2 \rangle}{2\Delta t}\), where the brackets \(\langle \rangle\) denote data averaged over all ellipsoids without the disturbance of others in a range of \((-10a, 10a)\) and fall into three different transverse \((y)\) separation regions (see Fig. 1), and \(\Delta x\) is the center-of-mass displacement along the channel axis and the angular displacement of the ellipsoid during time interval \(\Delta t = 0.1\) s.

All the values of \(D^T\) for different \(p\) and \(w\) are shown in Fig. 3, which shows the significant wall-drag effect of the Brownian diffusion: (i) \(D^T\) increases with \(w\), indicating that the wall-drag effect decreases. (ii) At \(p < 2.8\), \(D^T\) is almost unchanged with \(p\) but at \(p \geq 2.8\), \(D^T\) decreases with \(p\) (see Fig. 3). (iii) For the same \(p\) and \(w\), \(D^T\) decreases with increasing \(y/w\), indicating an increasing wall-drag effect, and the diffusion of particles is hindered.

The theoretical analysis of the wall-drag force caused by an upper-side open rectangular channel acting on a non-spherical particle has no analytic solution, although there are some exact solutions to some typical boundaries, and these solutions are only applicable to special configurations. We are interested in the low Reynolds number situations, as the Navier–Stokes equations become linear Stokes equations under the creeping motion approximation, and the drag force on the particle can be parameterized independent components caused by different walls. For this reason, approximate solutions for the modified drag force can be obtained, based on the so-called method of reflections.\[15\]

\[\text{The Brownian diffusion of a single particle in an unbounded quiescent fluid is well studied.}\[4\] Based on the Einstein relation, the diffusion coefficient can be formulated as \(D = k_B T/\gamma\), where \(\gamma\) is the drag coefficient, \(k_B\) is the Boltzmann constant, and \(T\) is the temperature of the fluid. For spherical particles, we have \(\gamma = 6\pi \eta R\), where \(\eta\) is the dynamic viscosity of the fluid, and \(R\) is the radius of the sphere. For a prolate ellipsoid with semi-axes \(a, b\) \((a > b)\), the diffusion coefficient can be described as \(D_i = k_B T/\gamma_i\), \(i = a, b, R_a, R_b, \gamma^a, \gamma^b, \gamma^{R_a}\), and \(\gamma^{R_b}\) are the translational and rotational drag coefficients of the ellipsoid about its long and short axes, respectively. We have \(\gamma^{a,b} = 6\pi \eta b G^{a,b}\) and \(\gamma^{R_a,R_b} = 6\pi \eta V G^{R_a,R_b}\), where \(V\) is the volume of the spheroid, and \(G\) is the geometric factor that renders the ellipsoid different relative to the case of a sphere. The geometric factors for prolate ellipsoids diffusing in unbounded 3D space are analyt-
ically derived from Perrin’s equations, \( G^\alpha(p) = \frac{8}{3} \left[ \frac{2p}{1 - p^2} + \frac{2p^2 - 1}{(p^2 - 1)^{3/2}} \right] \cdot \ln \left( \frac{p + \sqrt{p^2 - 1}}{p - \sqrt{p^2 - 1}} \right)^{-1}, \) \(^{(1)}\)

where \( p = a/b \) is the ellipsoid aspect ratio. If \( p = 1 \), then \( G^\alpha = 1 \) and \( \gamma^t \) reduce to the translational and rotational Stokes laws for a sphere.

However, for an anisotropic particle in a specific channel geometry, even the Reynolds number is very low, so the exact solutions for the effective wall-drag force are extremely complicated, and typically do not have a closed analytical form. In this work, a popular approach to approximate the solution is based on the method of reflections. The method of reflections is an iterative series solution technique, which decomposes the velocity and the pressure fields into a linear superposition of terms of successively higher order in the number of wall and sphere boundary interactions. The terms in the expansion are constrained to satisfy the boundary conditions alternately on the sphere and on the confining walls. \(^{(13)}\)

For this method, the expression of \( \gamma^\alpha \) (the model shown in Fig. 4) is obtained, which is usually in the form of a power series in \((b/l)\),

\[
\gamma^\alpha = 6\pi\eta b G^\alpha \sum_{i=0}^{\infty} \left[ k^T G^\alpha \frac{b_i}{l} \right]^i,
\]

\(^{(2)}\)

where \( l \) is the characteristic wall dimension, and \( k^T \) is a dimensionless constant, which depends on the geometry of the confinement. The values of \( k^T \) and \( l \) for typical boundaries have been intensively studied.\(^{(15)}\)

To the best of our knowledge, the values of \( k^T \) for an upper-side open rectangular groove have not been studied. Using a linear superposition of single-wall effects\(^{(3)}\) and the solutions of \( k^T \) for a single wall and between two walls, we obtain \( k^T = \frac{a}{b \eta} (c_1 \sqrt{T} + c_2 \sqrt{T}) \) for the upper-side open rectangular groove, where \( l = \sqrt{h_w}, \ c_1 = h/h' \) and \( c_2 = \left( \frac{1}{4} - \frac{1}{2} \frac{h_y}{h_w} \right)^{-1}, \ y \) is the transverse separation between the particle and the center of the groove.

\[\begin{array}{cccccc}
 & p = a/b & 1 & 1.8 & 2.2 & 2.8 & 5.2 & 7.5 \\
 & G^\alpha & 1 & 1.16 & 1.27 & 1.37 & 1.82 & 2.23 \\
 & D_0^T (\mu \text{m}^2/\text{s}) & 0.132 & 0.139 & 0.137 & 0.136 & 0.125 & 0.116 \\
\end{array}\]

\[^{(4,6,10)}\]

Table 1. Theoretical estimations of \( D^T \) in unbounded diluted solution for various aspect ratios \( p \) in our experiment.

by non-dimensionalizing the experimental \( D^T \) in Fig. 3 using the unbounded 3D diffusion coefficient \( D_0^T \). In our experimental system, the ellipsoid is strongly confined in the narrow channel, which leads to a small angle (\( \leq 8^\circ \)) between the long axis of the ellipsoid and the \( X \)-axis (Fig. 4(b)), indicating that the ellipsoid is almost parallel to the \( X \)-axis and the ellipsoid \( x \)-directional diffusion mainly appears along its long axis, thus in our experimental statistical results \( D^T \approx D^\alpha \), we set \( D_0^T = D_0^\alpha \). The constraint coefficient \( C^T \) is defined as

\[
C^T = \frac{D^T}{D_0^T} = \frac{k_{BT}/\gamma^\alpha}{k_{BT}/\gamma^\alpha} = \frac{6\pi\eta b G^\alpha}{6\pi\eta b G^\alpha \left[ \sum_{i=0}^{\infty} \left[ k^T G^\alpha \frac{b_i}{l} \right]^i \right]}.
\]

\(^{(3)}\)

The calculated \( C^T \) is explicit functions of the aspect ratio, channel shape and particle position.

In Fig. 5, the lines represent the theoretical prediction values of \( C^T \), which is calculated using Eq. (3). The filled and open symbols correspond to the experimental and simulation results, respectively. The channel width is \( w = 6 \mu \text{m} \). Figure 5 shows that our experimental results are in good agreement with the
theoretical prediction described above. It can be observed from Fig. 5 that: (1) under the same \(b/l\), \(C^T\) is inversely proportional to \(p\); (2) \(C^T\) decreases with the increase of \(y/w\). The experimental values of \(C^T\) are slightly smaller than the theoretical ones which may be caused by two factors: (i) the small angle between the long axis of the ellipsoid and the \(X\)-axis leads to a larger equivalent \(b\) when the ellipsoid diffuses along the \(x\)-direction; (ii) the nonzero angle leads to \(D^p\) being slightly larger than \(D^T\), i.e. the experimental \(C^T\) should be larger than the values plotted in Fig. 5.

To further elucidate the wall-drag effect of an isolated ellipsoid diffusing in an upper-side open rectangular groove, we performed finite element simulations using COMSOL Multiphysics v5.2a. The geometric parameters in the simulation were chosen to match the ellipsoids and the channel shape as used in our experiments. No-slip boundary conditions were set on ellipsoids and the surfaces of the channel, and open boundary conditions on the ends and upper side of the channel. The creep flow model in COMSOL was used and the particle was a rigid body. An axial velocity \(\nu\) was applied on the ellipsoid with different \(y/w\). Using the software, the drag force \(F_S\) of the ellipsoid under different conditions can be easily obtained. As mentioned earlier, \(C^T = F/F_S\). Finally, we quantitatively compared the simulation (shown by open symbols in Fig. 5) with the theoretical values and the experimental data.

Our experimental results clearly show that when a particle moves in a q1D channel, its diffusion behavior is severely restricted due to the reinforcement of the constraint, which is lower than the diffusion capacity under the q2D\(^6, 6\) constraint and furthermore lower than that in the infinite 3D space.\(^4\)

As shown in Fig. 5 and described above, \(C^T\) is inversely proportional to \(p\) for the same \(b/l\), and inversely proportional to \(b/l\) for the same \(p\). It results from the fact that when \(b/l\) is determined, a larger \(p\) means a larger \(a\), which leads to a greater wall-drag force, the same as for the situation where \(p\) is determined. Furthermore, we find that for the same \(p\) and \(w\), \(C^T\) decreases with the increase of \(y/w\). This can be explained such that with a larger \(y/w\), the particle gets closer to the side wall, thus the obstructive effect of the wall on particles is notably enhanced.

Compared with spherical particles diffusing in a narrow channel, whose motion is tightly confined to the center of the channel with very small transverse fluctuations,\(^{17}\) in our experiment, the ellipsoids are no longer confined to the center of the channel, and a stable stratification phenomenon was observed, which has rarely been discussed in literature related to spherical particles. For the ellipsoids, we find that for the same short axes \((b)\), the longer axes \((a)\) lead to a smaller diffusion capacity, and similarly, for the same \(a\), the larger \(b\) also results in less diffusion capacity, which is due to the hydrodynamic interaction between the ellipsoid particle and the channel wall. Due to the anisotropic shape of the ellipsoids and the deviation from the center of the channel, the hydrodynamic interaction is more complicated than that in spherical particles, although the ellipsoid is approximately parallel to the channel and the rotation is ignored.

Overall, for the case of an ellipsoid confined in an upper-side open rectangular channel, due to the strong geometric constraints, diffusive behavior of the particle is severely suppressed, especially for the transverse motion, and the long axis of the particle tends to be parallel to the channel.

In summary, the diffusion coefficients of ellipsoid particles diffusing in a channel have been verified by experiments and numerical simulation, and the prediction values are obtained using the method of reflections which independently superposes the wall-drag effects arising from each wall. All the results are in quantitative agreement, within the experimental precision, with those predicted using the method of reflections, which independently superposes the wall-drag effects arising from each wall. Studies have shown that the shape of the particle, the cross-section shape of the channel, and the relative position of the particle and the channel distinctly affect the Brownian motion of ellipsoids.

Ellipsoids are vertically stratified in the channel and remain stable, which has not been mentioned in the study of spherical particles diffusing in a channel.

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