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## Small Brownian objects self-align in nanofluidic channels

 Giulia Fiorucci,<sup>a</sup> Johan T. Padding,<sup>b</sup> and Marjolein Dijkstra<sup>\*a</sup>

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Although experiments and theory have widely investigated the self-alignment of asymmetric macro-sized objects (few tens of microns in size), the accessibility of much smaller length scales is still hindered by technical challenges. We combine Molecular Dynamics and Stochastic Rotation Dynamics techniques to investigate the self-orientation phenomenon at different length scales, covering from the micron to the nano scale by progressively increasing the relative strength of diffusion over convection. To this end, we model an asymmetric dumbbell particle in Hele-Shaw flow and explore a wide range of Péclet numbers (Pe) and different particle shapes, as characterized by the size ratio of the two dumbbell spheres ( $\tilde{R}$ ). By independently varying these two parameters we analyse the process of self-orientation and characterize the alignment of the dumbbell with the direction of the fluid flow. We identify three different trends of strong, weak and no alignment and we map out a state diagram in Pe versus  $\tilde{R}$  plane. Based on these results, we estimate dimensional length scales and flow rates for which these findings would be applicable in experiments. Finally, we find that the characteristic reorientation time of the dumbbell is a monotonically decreasing function of the dumbbell anisotropy.

### 1 Introduction

In recent years microfluidic devices have found increasingly wide application in several scientific areas<sup>1</sup>. They are widely employed in clinical and biological research for disease diagnosis<sup>2,3</sup> and for cytometric analysis<sup>4</sup>. For instance, microfluidic technology may be used to efficiently sort and analyse mixtures of healthy and diseased cells based on their differing physical properties<sup>5,6</sup>. Other applications are found in chemical and pharmaceutical industries, which use suspended micron-sized soft particles in confined flows as models to design deformable drugs delivery carriers<sup>7–10</sup>. The development of microfluidic technologies has opened new paths to manipulate suspended particles by having fine control over their position and orientation. Engineering particle trajectories in a device is now possible in three different ways, by means of external fields<sup>11</sup>, by taking advantage of hydrodynamic interactions in laminar flows, or by exploiting inertial effects in flow drag of finite Reynolds numbers<sup>12</sup>. The latter has been achieved with recent studies on flow sculpting<sup>13–15</sup>, while hydrodynamic interactions are exploited in laminar flows by engineering the geometry of the channel<sup>16–20</sup> or, alternatively, the shape of the sus-

pending particles<sup>21–23</sup>. This work is concerned with the last of these and specifically with dumbbell shaped particles. Such a particle, consisting of two connected disks, transported in a Hele-Shaw flow exhibits a rich variety of dynamic behaviours<sup>22</sup>, which are induced entirely by hydrodynamic interactions (HIs). By fine-tuning the relative size of the two disks, it is possible to control the trajectory of the particle. A comprehensive experimental and theoretical study is reported in Ref. [22], where the authors investigated the non-Brownian regime. A recent work has further analysed this particular system, providing an alternative and more efficient theoretical framework to solve the Stokes flow around the particle<sup>23</sup>. Their study focuses on the already known phenomenon of self-orientation, the spontaneous alignment of the long axis of the particle with the flow direction, provided that the two disks have different radii ( $R_1 \neq R_2$ ). This phenomenon originates from the hydrodynamic self-interaction, i.e. the hydrodynamic interactions the two disks exert on each other. In the present case of high confinement, a disk with diameter  $\sigma$  generates a flow disturbance which decays with distance  $r$  as a dipole field  $\propto \sigma/r^2$ . In addition, the magnitude of the generated velocity field linearly increases with the diameter of the disk. In case of a symmetric dumbbell, where the two disks have equal radii ( $R_1/R_2 = \tilde{R} = 1$ ), the hydrodynamic force that disk 1 exerts on disk 2 is perfectly balanced by the force disk 2 exerts on disk 1, resulting in only a lateral drift of the particle with-

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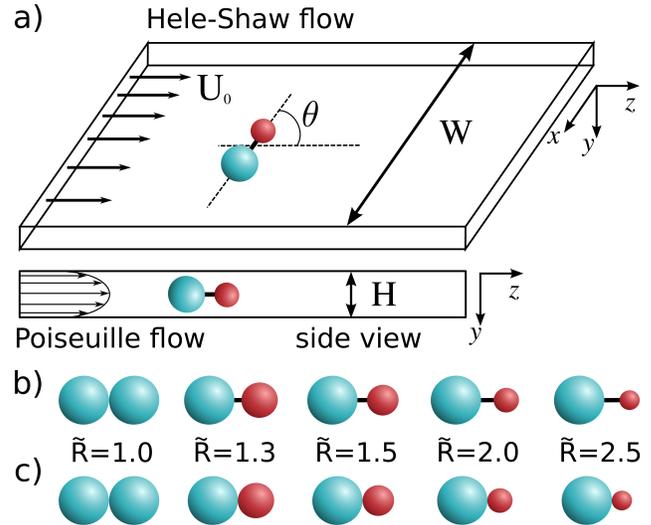
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out rotation. However if the dumbbell is asymmetric ( $R_1 > R_2$ ,  $\tilde{R} > 1$ ) the imbalance of internal hydrodynamic forces results in a torque on the dumbbell that must be balanced by a frictional torque of rigid rotation, which causes the small disk to be dragged downstream of the large disk. Although this specific system has been extensively examined, the studies performed so far concern macro-sized particles, which are considerably much less affected by thermal fluctuations as compared to colloids or polymer chains or macromolecules. The experiments<sup>22</sup> were performed at very high Pe number (of the order of  $10^4$ ), which was essential to drag particles of few tens of microns in width and 100 microns in length, dimensions that are quite big if compared to the typical colloidal length scales (100 – 1000 nm). Similarly, in numerical studies<sup>22–24</sup>, the lack of thermal noise in the deterministic model limits the investigations to ideally infinite Pe and do not provide insights on the possibility of self-orientation of smaller objects. On the basis of these arguments, natural questions arise: is the self-alignment still possible for nano-particles or macromolecules with an asymmetric conformation? What is the effect of thermal fluctuations on the self-orienting process? The progressively increasing interest in nanofluidics for "lab-on-a-chip" bioanalysis technology and for DNA manipulation<sup>25</sup>, leads to an urgent need to bridge these length scales and verify whether self-organization can still be exploited down to the nanoscale. In this study we show for the first time, at the best of our knowledge, that very small Brownian objects can exhibit self-alignment in nanofluidic channels. To do so, we combine Molecular Dynamics and Stochastic Rotation Dynamics techniques (MD+SRD) to simulate a dumbbell particle in a Hele-Shaw flow. This hybrid technique naturally includes hydrodynamic interactions as well as thermal fluctuations, and will be described in more detail in Section 2.2. In addition it enables us to arbitrarily tune the relative strength of the convection over the diffusion. This study aims to explore the Brownian regime where both thermal fluctuations and hydrodynamic interactions are important. In particular, we analyse the self-orientation phenomenon and the stability of the alignment with the flow by exploring a wide range of Péclet numbers, from the fully-Brownian regime towards the non-Brownian regime, and different particle shapes.

## 2 Model and Methods

### 2.1 The dumbbell in geometrical confinement

We perform numerical simulations (MD+SRD) to study the effect of Brownian fluctuations on the self-orientation process of a single dumbbell particle transported by a pressure-driven flow. In Figure 1 (a) we present a schematics of the system. We consider a shallow channel with a rectangular cross section. The confining walls are orthogonal to the  $x$  and  $y$  axes, while we implement periodic boundary conditions (PBC) along the  $z$  axis. The height of the channel is  $H$  and the width is  $W$ . The fluid flows with an approximately uniform maximal velocity  $U_0$  parallel to the  $z$  axis, as shown by the black arrows in the figure, and it drags the dumbbell particle embedded in the fluid. The dumbbell is composed of two colloidal spheres with radii  $R_1$  and  $R_2 \leq R_1$ . Note that we use spheres instead of disks as in Refs. [22,23],



**Fig. 1** Schematics of the system. Dumbbell particle flowing at the centre of a 3D channel of a rectangular cross section transported by the fluid flow at constant pressure gradient (a). Model of a dumbbell particle composed of two spheres of radius  $R_1$  and  $R_2 \leq R_1$ . We model five different dumbbell shapes by varying the sphere size ratio  $\tilde{R} = R_1/R_2$ . The center-to-center equilibrium distance  $s = 8.8 a_0$  is kept constant (b), or changes with  $\tilde{R}$  as  $s = R_1 + R_2$  (c). Note that the particle longitudinal axis can slightly wiggle in the  $yz$  plane, therefore we define the angle  $\theta \in (-180^\circ, 180^\circ]$  as the angle between the projection of the particle axis on the  $xz$  plane and the  $z$  axis.

because dumbbell spheres are simpler to simulate and easier to create experimentally at the small (colloidal) scales where Brownian motion is relevant. The spheres are bounded by a harmonic potential  $\beta U_h(r_{12}) = k (r_{12} - s)^2 / 2a_0^2$ , where  $\beta = 1/k_B T$  is the inverse temperature,  $k_B$  is the Boltzmann constant and  $T$  is the temperature. The instantaneous center-to-center distance of the spheres is  $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$ , with the spheres at positions  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , respectively. The parameter  $s$  denotes the equilibrium distance and  $a_0$  our unit of length, to be defined later. The parameter  $k$  is a dimensionless harmonic spring constant. We choose  $k = 10^5$  such that the characteristic period of elastic vibration of the dumbbell is much smaller than the time needed for the acoustic wave in the fluid to travel over the particle radius. The phenomenon of self-orientation depends sensitively on the shape of the particle, as characterized by the size ratio  $\tilde{R} = R_1/R_2$ . To investigate the effect of particle shape on the hydrodynamic self-orientation, we consider dumbbells with five different size ratios. The radius of the cyan sphere  $R_1$  is kept constant, whereas the radius of the red sphere  $R_2$  is varied. We test two models, in the first  $s$  is held constant for different size ratios at a value of  $8.8 a_0$ , while in the second  $s = R_1 + R_2$ , as illustrated in Figures 1(b) and (c), respectively. The interaction between each sphere of the dumbbell and the confining walls is described by a purely repulsive Weeks-Chandler-Andersen (WCA) potential<sup>26</sup>

$$\beta \phi_{cw}(r_i) = \begin{cases} 4\beta \epsilon_{cw} \left[ \left( \frac{\sigma_{cw}}{r_i} \right)^{12} - \left( \frac{\sigma_{cw}}{r_i} \right)^6 + \frac{1}{4} \right] & r_i \leq 2^{1/6} \sigma_{cw} \\ 0 & r_i > 2^{1/6} \sigma_{cw}, \end{cases} \quad (1)$$

where  $r_i$  is the distance along  $i = \{x, y\}$  between the center of the sphere and the surface of the wall,  $\epsilon_{cw} = 40 k_B T$  sets the colloid-wall energy scale and  $\sigma_{cw}$  represents the colloid-wall collision radius. The dimensions of the channel are  $W \times H = 100 \times 10 a_0^2$ . The length of the channel along the  $z$  direction,  $L_z$ , is chosen to be sufficiently large that the hydrodynamic interactions of the dumbbell particle with its own periodic image can be neglected. In a quasi-2D system, the flow disturbance generated by the presence of the particle decays as  $\sigma^2/r^2$ , hence the disturbance is less than 0.1% for  $r = 50 \sigma$ , and with a typical  $\sigma$  of  $8 a_0$  we therefore choose  $L_z = 400 a_0$ . We choose  $\sigma_{cw} = 4.4 a_0$  for the largest sphere, such that it is highly confined in the  $y$  direction, leaving a lubricating gap of  $0.6 a_0$  to the wall. Position  $\mathbf{R}_i$  and velocity  $\mathbf{V}_i$  of each sphere  $i$  are integrated via the velocity Verlet algorithm<sup>27</sup>

$$\mathbf{R}_i(t + \Delta t_{MD}) = \mathbf{R}_i(t) + \mathbf{V}_i(t) \Delta t_{MD} + \frac{\mathbf{F}_i(t)}{2M_i} \Delta t_{MD}^2, \quad (2)$$

$$\mathbf{V}_i(t + \Delta t_{MD}) = \mathbf{V}_i(t) + \frac{\mathbf{F}_i(t) + \mathbf{F}_i(t + \Delta t_{MD})}{2M_i} \Delta t_{MD}, \quad (3)$$

over a timestep  $\Delta t_{MD}$ .  $\mathbf{F}_i(t)$  is the force acting on sphere  $i$  at time  $t$  and  $M_i$  is the mass of the sphere. We match the mass density of each dumbbell bead with the mass density of the fluid.

## 2.2 The fluid

The MD+SRD method was introduced by Malevanets and Kapral in 1999<sup>28,29</sup>. Since then it has been implemented to study a large variety of systems. For example, it has been employed to study the fluid flow in confinement, or driven by an external force<sup>30</sup>. In addition, it has been applied to investigate polymers in solution<sup>31</sup> or the sedimentation in colloidal suspensions<sup>32</sup>. Moreover this technique is particularly convenient for the study of colloidal suspensions embedded in a fluid, since the intrinsically stochastic nature of the algorithm naturally incorporates the thermal noise<sup>28</sup>, i.e. it automatically captures the Brownian fluctuations experienced by the colloidal particles in a suspension. Within MD+SRD the fluid is represented by the explicit presence of coarse-grained point particles of mass  $m_f$ , whose positions and velocities are continuous variables in space. Hence we refer to these point particles as “fluid particles”, even if the physical properties of the fluid are not represented at the single particle level, but are rather extracted from a local average. Fluid particles are subjected to Newton’s laws of motion and their positions and velocities are integrated via the MD scheme. This is the streaming step of the simulation method, where we implement the velocity Verlet algorithm<sup>27</sup>

$$\mathbf{r}_i(t + \Delta t_{MD}) = \mathbf{r}_i(t) + \mathbf{v}_i(t) \Delta t_{MD} + \frac{\mathbf{f}_i(t)}{2m_f} \Delta t_{MD}^2, \quad (4)$$

$$\mathbf{v}_i(t + \Delta t_{MD}) = \mathbf{v}_i(t) + \frac{\mathbf{f}_i(t) + \mathbf{f}_i(t + \Delta t_{MD})}{2m_f} \Delta t_{MD}, \quad (5)$$

where  $\Delta t_{MD}$  is the integration time step,  $\mathbf{r}_i$  and  $\mathbf{v}_i$  are, respectively, the position and the velocity of particle  $i$ , which is subject to the total force  $\mathbf{f}_i$ . In the streaming step fluid particles do not interact with each other and behave as an ideal gas. Therefore the total force acting on a fluid particle arises from the colloid-fluid interaction and the pressure gradient imposed externally. While

executing the collision step, the SRD algorithm enables the exchange of momentum throughout the solvent performing coarse-grained collisions among the fluid particles. Every time interval  $\Delta t_c = 4 \Delta t_{MD}$  we partition the volume of the system into cubic cells (SRD cells of size  $a_0^3$ ), we compute the center of mass velocity  $\mathbf{v}_{cm}$  in each cell, and we rotate the relative velocities by a fixed angle  $\alpha = \pi/2$  about a randomly oriented axis<sup>33</sup>

$$\mathbf{v}_i^{new} = \mathbf{v}_{cm} + \mathcal{R}(\alpha) \times (\mathbf{v}_i^{old} - \mathbf{v}_{cm}), \quad (6)$$

where  $\mathbf{v}_i^{old}$  and  $\mathbf{v}_i^{new}$  are the velocities of particle  $i$  before and after the collision step, respectively, and  $\mathcal{R}$  is the rotation matrix. We shift the SRD cells before performing the collision step, in order to maintain Galilean invariance<sup>34,35</sup>. The SRD method locally conserves both energy and momentum, which is crucial for correctly reproducing the Navier-Stokes hydrodynamics<sup>28</sup>. In order to generate a fluid flow, as shown in Figure 1, we apply an external driving force on the fluid particles. The force is parallel to the  $z$  direction. In order to maintain a constant temperature of the fluid, we implement a modified version of the stochastic thermostat proposed by Heyes<sup>36</sup>, which is extensively described in Ref. [37]. To ensure the velocity of the fluid is zero at the wall, we impose no-slip boundary condition by implementing the bounce-back rule<sup>28</sup>. In order to prevent spurious slip, we also insert virtual particles into the SRD cells that are overlapping with the wall when performing the collision step<sup>30</sup>. The fluid is represented by  $N_f = 2 \times 10^6$  particles corresponding to a mass density  $\rho_f = 5 m_f / a_0^3$ . The fluid particles interact with the dumbbell through the repulsive WCA potential

$$\beta \phi_{cf}(r) = \begin{cases} 4\beta \epsilon_{cf} \left[ \left( \frac{\sigma_{cf}}{r} \right)^{12} - \left( \frac{\sigma_{cf}}{r} \right)^6 + \frac{1}{4} \right] & r \leq 2^{1/6} \sigma_{cf} \\ 0 & r > 2^{1/6} \sigma_{cf}, \end{cases} \quad (7)$$

where  $\epsilon_{cf} = 2.5 k_B T$  sets the colloid-fluid energy scale and  $\sigma_{cf}$  is the colloid-fluid collision radius. We remark that  $\sigma_{cf}$  should be smaller than  $\sigma_{cw}$  to prevent the effect of spurious depletion that might arise between colloid and wall<sup>33</sup>. Therefore we impose  $\sigma_{cw} = 1.1 \sigma_{cf}$ . In addition, we highlight that we implement the slip boundary condition on the surface of the colloidal particle; this property naturally comes from the isotropic property of the colloid-fluid interaction potential.

The different hydrodynamic regimes are characterised by dimensionless numbers that determine the relative importance of the different physical processes. The dependence of these dimensionless numbers on the simulation parameters are described in Ref. [33]. First, we ensure that the fluid modelled by SRD particles reproduces a liquid-like rather than a gas-like dynamics. The Schmidt number distinguishes between these two different behaviours, being defined as  $Sc = \nu / D_f$  the rate of diffusive momentum transfer over the rate of diffusive mass transfer in the fluid. When momentum transfer results from collisions among particles rather than mass diffusion, the SRD fluid represents a liquid and  $Sc \gg 1$ . In our simulations  $Sc > 6$  is sufficiently high to guarantee a liquid-like dynamics. Second, we ensure that the Mach number<sup>38</sup>  $Ma = U_0 / c_f$ , which compares the velocity of the fluid  $U_0$  with respect to the speed of sound  $c_f$ , is small enough

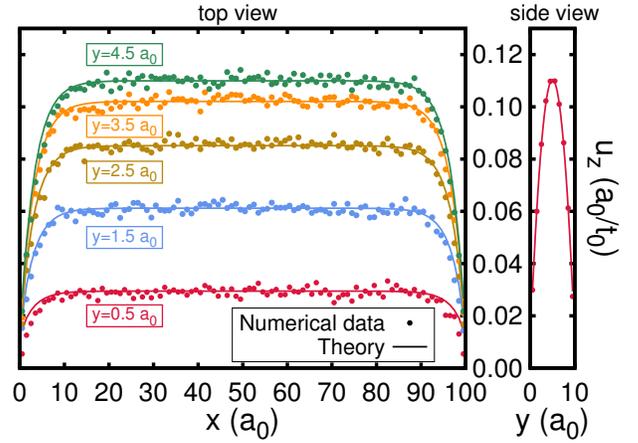
to avoid compressibility effects so that the fluid can be assumed to be effectively incompressible. Hence, we set  $Ma \sim 0.1$  in our simulations. Another important parameter is the Reynolds number<sup>38</sup>  $Re = U_0 \sigma_{cf} \rho_f / \eta$  which measures the relevance of inertial over viscous forces and where  $\eta$  denotes the shear viscosity of the fluid. We simulate a fluid in the Stokes regime, i.e. in absence of turbulence. The critical Reynolds number  $Re_c$ , which discriminates the crossover from laminar to turbulent flow, depends on the physical system under investigation. It is known that  $Re_c \sim 1$  in bulk<sup>33</sup> while it has been recently shown that the critical threshold is higher in a channel ( $Re_c \sim 800$ )<sup>39</sup> and much higher in a pipe ( $Re_c \sim 2000$ )<sup>40</sup>. In our simulations  $Re < 0.8$ , which corresponds to Stokes flow. In the present work we perform simulations exploring a wide range of Péclet numbers. This parameter measures the relevance of convective over diffusive transport, and we define it as follows

$$Pe = \frac{U_0 R_1}{D_0}, \quad (8)$$

where  $R_1$  and  $D_0$  are, respectively, the radius and the bare diffusion coefficient of the larger sphere. We chose  $R_1$  as a representative quantity for the size of the dumbbell since it does not vary with size ratio  $\bar{R}$ , implying that  $Pe$  and  $\bar{R}$  can be varied as independent parameters. To explore different hydrodynamic regimes, we vary the shear viscosity of the fluid  $\eta$ . More specifically in terms of simulation parameters, we change the integration time step from  $\Delta t_{MD} = 0.025 t_0$  for  $Pe \sim 40$ , to  $\Delta t_{MD} = 1.75 \times 10^{-3} t_0$  for  $Pe \sim 500$ , being  $t_0 = a_0 \sqrt{m_f / k_B T}$ . With this choice of parameters the shear viscosity varies from  $\eta = 2.5 \eta_0$  to  $\eta = 32 \eta_0$ , respectively, being  $\eta_0 = m_f / (a_0 t_0)$ .

### 2.3 Achieving steady state flow of the fluid

During the self-orientation process the asymmetric dumbbell changes its orientation and eventually aligns with the fluid flow with the small sphere dragged downstream of the large sphere. This phenomenon is determined by the hydrodynamic self-interaction, while the hydrodynamic interaction with the side walls (the walls orthogonal to the  $x$  axis) plays no role in this process<sup>22</sup>. We position the particle's center of mass at the center of the channel  $x = 0$ , with orientation  $\theta = 170^\circ$ , where  $\theta \in (-180^\circ, 180^\circ]$  is defined as the angle between the projection of the particle's long-axis on the  $xz$  plane and the  $z$  axis (see Figure 1(a)). Before proceeding with the measurements of the angle  $\theta$  over time, we wait till the fluid forms the expected velocity profile. In order to achieve this steady state without affecting the initial orientation of the dumbbell, we initially impose a constraint on the dumbbell, such that the acceleration of the two spheres along the  $y$  and the  $z$  axes are the same, while the acceleration of the center of mass along the  $x$  axis is zero. This can be achieved by imposing the following forces on the large particle (here with



**Fig. 2** Velocity profile of the fluid flow  $u_z$  along  $x$  and  $y$  at different heights. The dots represent the results obtained with the MD+SRD method, while solid lines are theoretical predictions. The profile is determined by the geometry of the channel. In this shallow channel we observe almost a flat profile (Hele-Shaw flow) from the top view, where different colors denote velocity profiles at different heights along the  $y$  axis, and a parabolic profile (Poiseuille flow) from the side view, where we show the profile at  $x = 50.0 a_0$ .

label 1)

$$\begin{aligned} F_{x1}^{new} &= F_{x1} - \frac{\mu}{M_2} (F_{x1} + F_{x2}) \\ F_{y1}^{new} &= \frac{\mu}{M_2} (F_{y1} + F_{y2}) \\ F_{z1}^{new} &= \frac{\mu}{M_2} (F_{z1} + F_{z2}), \end{aligned} \quad (9)$$

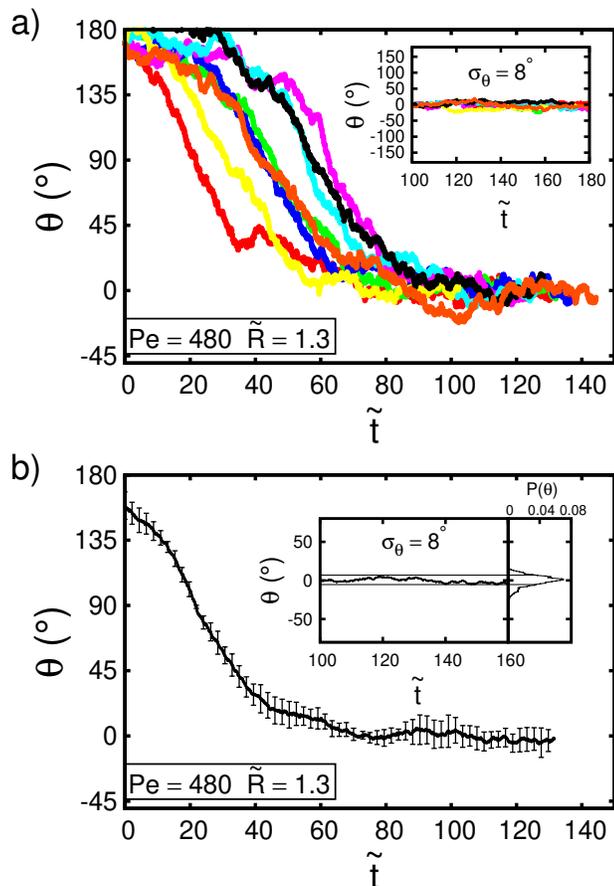
where  $\mu = M_1 M_2 / (M_1 + M_2)$  is the reduced mass,  $M_j$  is the mass of sphere  $j$  and  $F_{ij}$  is the instantaneous force along  $i$  experienced by sphere  $j$ . Similarly, the forces imposed on the small particle (labelled 2) can be obtained from (9) by exchanging the subscripts 1 and 2. Once the expected velocity profile is formed, we release the constraints and start our measurements. The velocity profile of the fluid along the  $z$  direction is determined by the specific geometry of the channel. In our case, we expect to observe a parabolic profile (Poiseuille flow) from the side view because of the high confinement in the  $y$  axis, while we expect an approximately uniform profile (Hele-Shaw flow) from the top view.

## 3 Results

### 3.1 Verification of fluid velocity profile

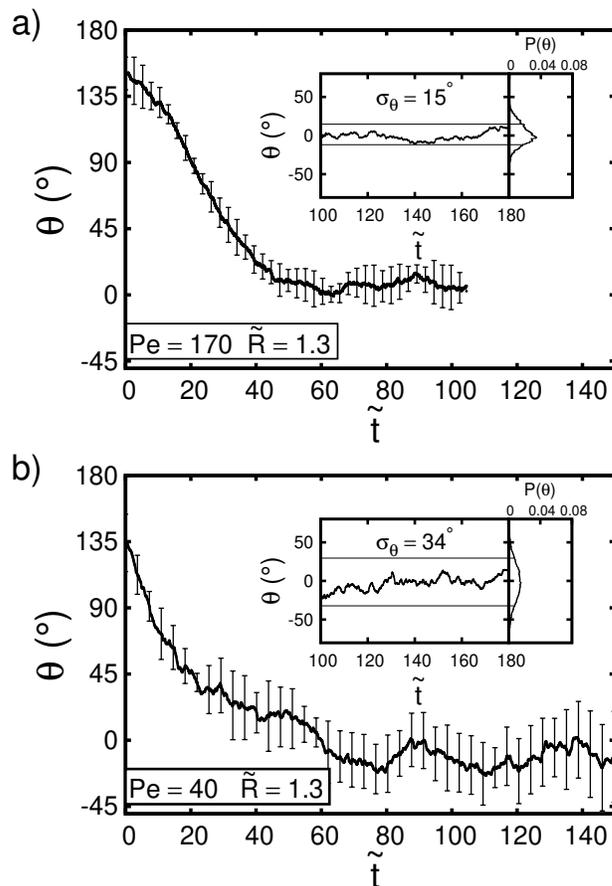
In Figure 2 we report the fluid velocity profile  $u_z$  from the top view at different heights  $y$  of the channel, and from the side view at  $x = 50 a_0$ . The points represent our numerical results, obtained by averaging the velocities of the fluid particles over the volume of a single SRD cell ( $a_0^3$ ). The profiles are in very good agreement with the theoretical prediction<sup>41</sup>, represented here by the solid lines. We highlight that there is no adjustable parameter for the magnitude of the velocity field. However, our profile extrapolates to a finite non-zero velocity at the wall, and therefore we obtain the best fit by including a small slip velocity of magnitude  $\sim 0.01 a_0 / t_0$ .

### 3.2 Hydrodynamic self-orientation: the state diagram



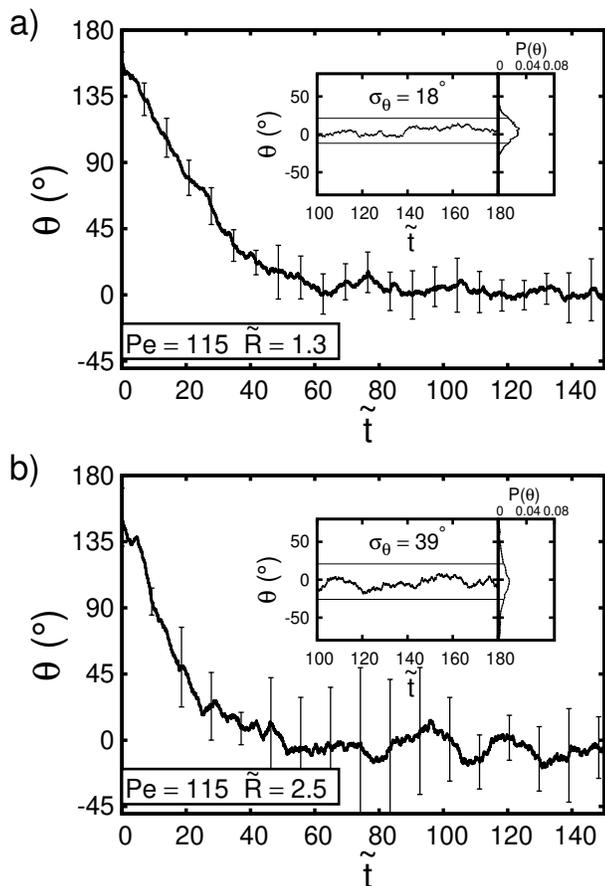
**Fig. 3** (a) The angle  $\theta$  of the long-axis of the dumbbell with the flow direction as a function of reduced time  $\tilde{t} = tU_0/s$  for a dumbbell with  $s = 8.8 a_0$  and size ratio  $\tilde{R} = 1.3$  in a channel under an external flow at  $Pe = 480$ . Different curves represent independent runs. The graph shows the self-orientation process where the particle is initially positioned with  $\theta = 170^\circ$  and, due to the hydrodynamic self-interaction, it eventually aligns with the fluid flow ( $\theta = 0^\circ$ ). The inset shows fluctuations of  $\theta$  about the equilibrium value  $\theta = 0^\circ$  as a function of  $\tilde{t}$  for simulation runs where the dumbbell is initially positioned with  $\theta = 0^\circ$ . We measure the standard deviation of  $\theta$  obtaining  $\sigma_\theta = 8^\circ$ . (b) Average of  $\theta$  over eight runs presented in (a). Inset: the left panel shows the average of  $\theta$  over eight runs in (a), the right panel shows the normalised histogram of  $\theta$ . The horizontal lines indicate the full width at half maximum.

We perform MD+SRD simulations on a single dumbbell particle with fixed  $s = 8.8 a_0$  as shown in Figure 1(b) in a fluid flow. We study the self-orientation process by measuring the angle  $\theta$  of the long-axis of the dumbbell with the flow direction as a function of time. Note that our model consists of a dumbbell in three dimensions which can slightly wiggle in the  $yz$  plane. Hence the angle  $\theta$  is defined as the angle between the  $xz$  projection of the particle center-to-center axis and the  $z$  axis. For example, we plot the angle  $\theta$  as a function of the reduced time  $\tilde{t} = tU_0/s$  for  $Pe = 480$  and  $\tilde{R} = 1.3$  in Figure 3(a). Each curve in the plot represents a single run performed at the same physical conditions. We simulated eight independent runs in order to investigate the statistical fluctuations. All the curves show essentially the same trend. The simulation is initiated with a dumbbell particle forming an an-



**Fig. 4** The average of  $\theta$  over eight realizations as a function of reduced time  $\tilde{t} = tU_0/s$  for a dumbbell with  $s = 8.8 a_0$  and size ratio  $\tilde{R} = 1.3$  in a channel under an external flow at  $Pe = 170$  (a) and  $Pe = 40$  (b). By decreasing  $Pe$  the curves presents larger fluctuations and  $\sigma_\theta$  increases, being  $\sigma_\theta = 15^\circ$  in (a) and  $\sigma_\theta = 34^\circ$  in (b).

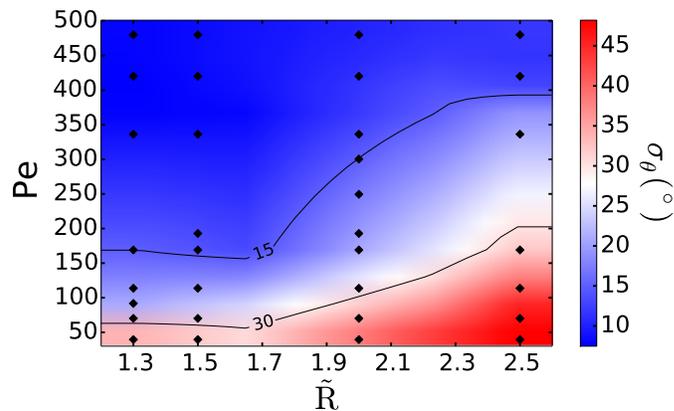
gle  $\theta = 170^\circ$  with the direction of the fluid flow. After a certain waiting time, the value of  $\theta$  rapidly decreases towards  $\theta = 0^\circ$ , where it remains stable over time within small fluctuations due to the thermal noise. Note that at this apparently high  $Pe$  Brownian fluctuations are still visible, but, contrary to the case of the Brownian regime, they do not significantly interfere with the hydrodynamic drag and the resulting particle orientation. The thermal noise is not only the cause of the small fluctuations about the equilibrium orientation at  $\theta = 0^\circ$  but it also prevents the immediate reorientation of the dumbbell: the configuration characterized by  $\theta = 180^\circ$  is an unstable equilibrium configuration<sup>22</sup>, therefore the hydrodynamic torque about this angle is still quite weak compared to the Brownian fluctuations. Consequently, the competition between the hydrodynamic torque, which leads to the reorientation of the particle, and the Brownian fluctuations, determines the different waiting times at which the particle starts reorienting. In Figure 3(a) we clearly observe this phenomenon by comparing eight independent runs. Nevertheless the different waiting times do not affect the self-alignment process itself. Once the hydrodynamic forces start to dominate, the change in  $\theta$  with time for intermediate angles is very similar in the eight runs. This is most clearly appreciated by the similarity of the



**Fig. 5** The average of  $\theta$  over eight realizations as a function of reduced time  $\tilde{t} = t U_0/s$  for a dumbbell with  $s = 8.8 a_0$  and size ratio  $\tilde{R} = 1.3$  (a) and  $\tilde{R} = 2.5$  (b) in a channel under an external flow at  $Pe = 115$ . By increasing  $\tilde{R}$  the curves exhibit larger fluctuations and  $\sigma_\theta$  increases, being  $\sigma_\theta = 18^\circ$  in (a) and  $\sigma_\theta = 39^\circ$  in (b).

slopes around  $\theta = 90^\circ$ , in fact the typical time scale of the self-orientation process is only intrinsically related to the shape of the particle, parametrized here by  $\tilde{R}$ , and the geometry of the channel. Later in this section we will provide quantitative results on this topic, while for the moment we focus on the alignment of the particle once the self-orientation has occurred. Specifically, we investigate how the alignment is destabilized by the thermal fluctuations as we decrease the Péclet number. In addition, we show that as we enter the Brownian regime, the stability of the alignment depends also on the shape of the particle, therefore we will also compare the behaviour at constant  $Pe$  and different  $\tilde{R}$ .

As we lower the Péclet number we enhance the strength of the thermal noise relative to the strength of the convective flux. We compare Figures 3(b), 4(a) and 4(b) where we show the average of  $\theta$  over eight realizations as a function of time, for  $\tilde{R} = 1.3$  and  $Pe = 480$ ,  $Pe = 170$  and  $Pe = 40$ , respectively. It is apparent that the curves present larger errorbars as we lower the Péclet number, moreover the fluctuations in orientation about the equilibrium position  $\theta = 0^\circ$  are more pronounced. To quantify the magnitude of these oscillations we measure the standard deviation of the angle  $\theta$  with respect to its mean value  $\langle \theta \rangle$  as  $\sigma_\theta = \sqrt{\langle \theta^2 \rangle - \langle \theta \rangle^2}$ . By decreasing  $Pe$ , we observe an increase of  $\sigma_\theta$ , as shown in the



**Fig. 6** State diagram of a dumbbell with  $s = 8.8 a_0$  describing the stability of the particle self-alignment along the direction of the fluid flow for different Péclet numbers  $Pe$  and size ratios  $\tilde{R}$ . The characterization of stability is based on the magnitude of the standard deviation  $\sigma_\theta = \sqrt{\langle \theta^2 \rangle - \langle \theta \rangle^2}$  of  $\theta$  with respect to its mean value  $\langle \theta \rangle$ . The blue region denotes oscillations limited to  $\sigma_\theta \leq 15^\circ$ , where the alignment is strong. The light blue region is characterized by oscillations  $15^\circ < \sigma_\theta \leq 30^\circ$  so the alignment is weaker. Finally, the red region denotes oscillations with  $\sigma_\theta > 30^\circ$ , therefore the alignment is no longer possible in this region. The black dots denote the state points at which the simulations were performed. The heatmap is computed by linear interpolation between these points. The black lines delimit the three regimes of alignment.

inset of Figures 3(b) and 4. Here we also display the histogram of  $\theta$ , which broadens up as  $Pe$  decreases. This is clear evidence that decreasing the Péclet number destabilizes the alignment of the particle at  $\theta = 0^\circ$ , which is the hydrodynamically stable configuration.

The Péclet number is a good parameter to estimate the relevance of the thermal fluctuations compared to the hydrodynamic drag, but it is not sufficient to give a complete description of the stability of the particle. From the definition given in Equation (8) it is clear that  $Pe$  does not depend on the specific shape of the particle, only on its typical length scale. However we expect that the stability is also related to the shape of the dumbbell. For instance we intuitively expect that as we decrease the radius of sphere 2, the thermal fluctuations become more effective, leading to destabilization. We therefore investigate also the behaviour of the dumbbell by allowing  $\tilde{R}$  to vary while we keep  $Pe$  constant. In analogy to the previous analysis, we compare the fluctuations around  $\theta = 0^\circ$  for different  $\tilde{R}$ . In Figure 5 we show the average of  $\theta$  as a function of time for  $Pe = 115$  and size ratio  $\tilde{R} = 1.3$  (a) and  $\tilde{R} = 2.5$  (b). As expected, we observe larger fluctuations as we increase the size ratio  $\tilde{R}$ : we estimate that  $\sigma_\theta = 18^\circ$  for  $\tilde{R} = 1.3$ , while  $\sigma_\theta = 39^\circ$  for  $\tilde{R} = 2.5$ .

In order to investigate how thermal fluctuations destabilize the alignment of the particle as we vary both the Péclet number and the size ratio, we ran many simulations for  $40 \lesssim Pe \lesssim 500$  and for  $1.0 < \tilde{R} \leq 2.5$ . By analysing the fluctuations of the angle  $\theta$  about the equilibrium position  $\theta = 0^\circ$ , we discriminate three different regimes for the hydrodynamic self-alignment. Our results are summarized in Figure 6. The black dots display the simulation runs performed at a specific value of  $Pe$  and  $\tilde{R}$ . We compute the  $\sigma_\theta$  for each run and linearly interpolate between points to obtain

a heatmap. The blue region represents the regime of strong alignment, where  $\sigma_\theta \leq 15^\circ$ . We delimit this region with a solid black line corresponding to  $\sigma_\theta = 15^\circ$ . The light blue region represents the regime of weak alignment, where  $15^\circ < \sigma_\theta \leq 30^\circ$ . Finally, the red region shows the regime of no alignment, where  $\sigma_\theta > 30^\circ$ , also here delimited by a black line corresponding to  $\sigma_\theta = 30^\circ$ . For a sufficiently high Péclet number,  $Pe \geq 400$ , a change in the size ratio does not affect the self-orientation process of the dumbbell, as the convective flux leads to a strong hydrodynamic torque. We define this range of high  $Pe$  as the non-Brownian regime. For  $Pe < 50$  the self-orientation does not occur for any size ratio of the dumbbell. Therefore we define this regime as the Brownian regime. In the intermediate  $Pe$  regime, i.e.  $50 \leq Pe < 400$ , we find all three self-orientation behaviours: upon increasing  $\tilde{R}$ , the strong alignment region shrinks, whereas the weak and no alignment regions widen. This confirms our expectations that the stability is also strongly related to the shape of the dumbbell, and provides a quantitative estimation of this dependence. We note that small changes in angle cut-offs for defining the stability regions can determine a small shift of the boundaries, but the overall trends remain the same.

On the basis of these results, we can extract informations on the required experimental conditions to achieve a certain level of alignment. In Table 1 are listed several values of particle's radius, which ranges from few microns for a macro-colloid, down to fractions of micron for nanoparticles and even smaller for macromolecules. For each value we compute the dimensions of the channel and the critical flow rate  $U_0^c$ . The latter quantity is the minimum fluid velocity required to obtain a certain level of alignment. For instance, a particle with  $R_1 = 0.1 \mu m$  and  $\tilde{R} < 1.5$  displays weak alignment for  $U_0^c \geq 1 \times 10^3 \mu m$  and  $U_0^c < 3 \times 10^3 \mu m$ , while it shows strong alignment for  $U_0^c \geq 3 \times 10^3 \mu m$ . In order to observe strong alignment of particle with same size and  $\tilde{R} = 2.5$ , ones has to set a flow rate  $U_0^c \geq 9 \times 10^3 \mu m$ . The critical flow rates are derived by inverting equation (8), obtaining

$$U_0^c = \frac{Pe^c k_B T}{6\pi\eta R_1^2}, \quad (10)$$

where  $Pe^c$  is the minimum value of  $Pe$  required to obtain a certain level of alignment and  $D_0$  is rewritten in terms of the fluid viscosity through the Stokes-Einstein equation  $D_0 = k_B T / (6\pi\eta R_1)$ . In our computation we considered room temperature  $T = 300 K$  and the viscosity of water  $\eta = 0.001 Pa s$ .

$R_1$ ( $\mu m$ )	$W$ ( $\mu m$ )	$H$ ( $\mu m$ )	$U_0^c$ ( $\mu m/s$ )
10	250	25	$(1, 3, 9) \times 10^{-1}$
1	25	2.5	$(1, 3, 9) \times 10^1$
0.1	2.5	0.25	$(1, 3, 9) \times 10^3$
0.01	0.25	0.025	$(1, 3, 9) \times 10^5$
			$Pe^c = (50, 150, 400)$

**Table 1** Critical flow speed  $U_0^c$  for different particle's sizes  $R_1$  and for different regimes of alignment ( $Pe^c$ ). We also display width  $W$  and height  $H$  of the channel for each particle's size.

### 3.3 Hydrodynamic self-orientation: the relaxation time

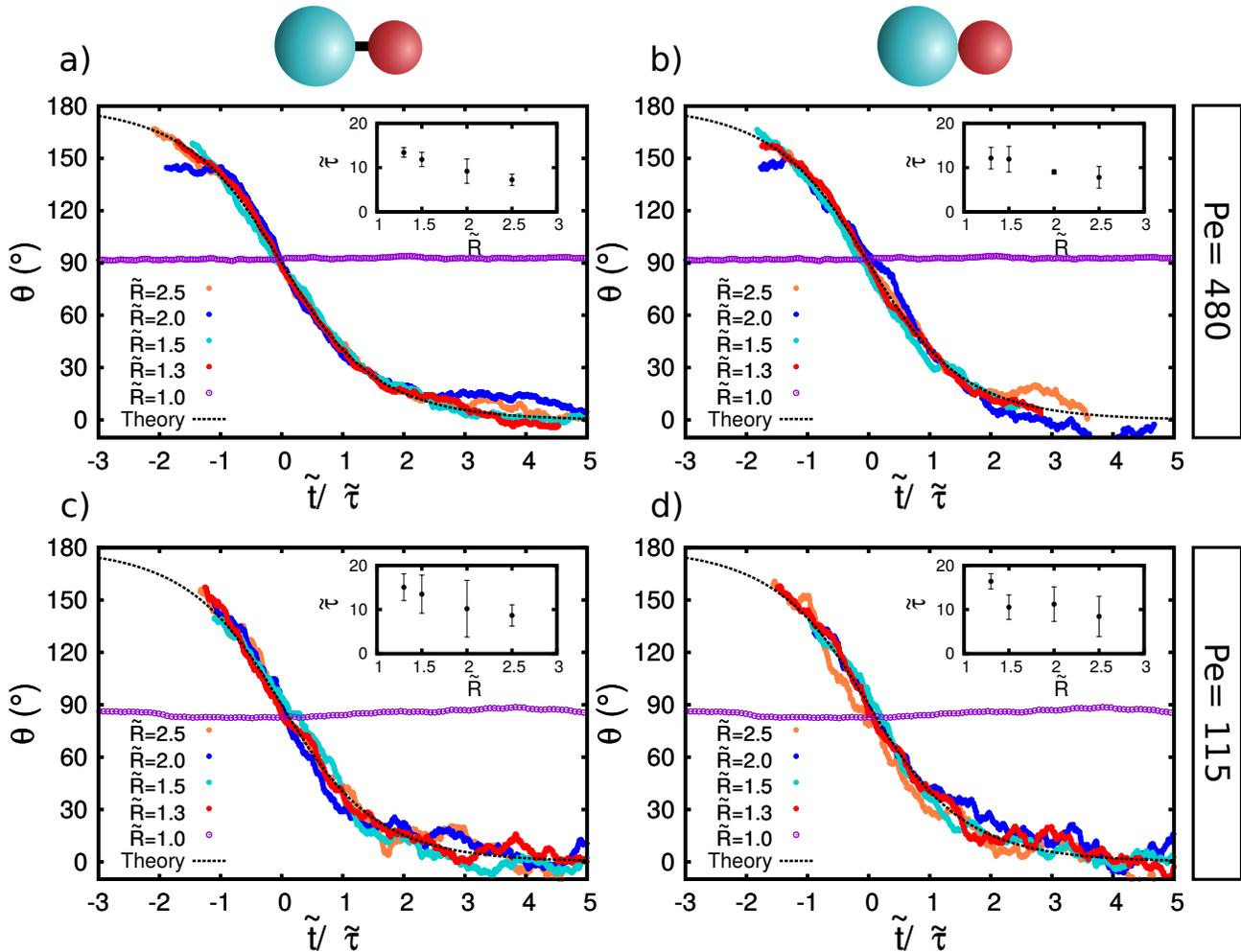
As mentioned earlier, in this section we provide a quantitative analysis of the rate of the self-orientation process. An analytical expression describing how  $\theta$  evolves with time  $\tilde{t}$  was derived for the case of a dumbbell particle composed of two disks instead of two spheres<sup>22</sup>. Even though the two dumbbell models are different, the analytical expression is valid also for the present case of a dumbbell composed of spheres. In fact it has recently been shown that the analytical expression holds for all particles which have the property to be mirror symmetric with respect to the  $xy$  plane passing through their longitudinal axis<sup>24</sup>. Taking  $\tilde{t} = 0$  when  $\theta = 90^\circ$ , the dependence of  $\theta$  with respect to  $\tilde{t}$  can be expressed implicitly as<sup>22</sup>

$$\tilde{t} = \tilde{\tau} \ln \left( \frac{1 + \cos(\theta)}{\sin(\theta)} \right), \quad (11)$$

where  $\tilde{\tau}(\tilde{R}, H, W)$  is the relaxation time defined as the characteristic time the particle spends in self-orienting from  $\theta = 90^\circ$  to  $\theta = 0^\circ$ . This parameter depends on the shape of the particle and the geometry of the channel. This quantity can be extracted by fitting equation (11) to the data obtained from the numerical simulations. Each simulation run is parametrized by  $Pe$  and  $\tilde{R}$ . We perform eight independent runs to carry out our statistical analysis.

To perform the fit, we first shift each single curve  $\theta(\tilde{t})$  in time, such that  $\theta = 90^\circ$  corresponds to  $\tilde{t} = 0$ . It is worth to mention that the time shift is usually different for each curve. This is due to the time delay the particle accumulates before starting the self-orientation. We shift the curves also to perform an accurate averaging of  $\theta$  over the eight realizations. In fact, this procedure guarantees that we get the best superpositions of the curves for different runs, as the internal hydrodynamic torque is maximal at  $\theta = 90^\circ$ . We obtain the value of  $\tilde{\tau}$  by fitting equation (11) on a single realization. We then average the values of  $\tilde{\tau}$  obtained over eight runs. In Figure 7(a) we show the decay of the average of  $\theta$  over the eight realizations as a function of time for different  $\tilde{R}$  at  $Pe = 480$ , in the non-Brownian regime. Since time is scaled by  $\tilde{\tau}$ , all curves collapse onto the theoretical master curve. The match with theory is remarkably good. In the inset we represent the values of  $\tilde{\tau}$  for different size ratio  $\tilde{R}$ . The characteristic time of alignment monotonically decreases with increasing size ratio. In fact as the size ratio starts to increase from  $\tilde{R} = 1.0$ , the hydrodynamic torque also increases leading to a faster convergence to the equilibrium configuration. A similar trend is shown in Figure 7(c) where we illustrate the same analysis performed at  $Pe = 115$ , in the intermediate regime. We highlight that the only noticeable difference is the presence of small fluctuations within the curves which denotes the relative importance of thermal noise over the hydrodynamic convective drag with respect to the case of the non-Brownian regime. These insets also show that the relaxation time for self-alignment is mostly a function of particle geometry, and not of Péclet number, for intermediate to large Péclet numbers.

We also analyse the robustness of the model with respect to small changes in the design of the dumbbell particle. More specifically, we performed simulations with the model presented in Fig-



**Fig. 7** The average of  $\theta$  as a function of rescaled time  $\tilde{t}/\tilde{\tau}$ . Each coloured curve represents a different size ratio  $\tilde{R}$  and is obtained by averaging over eight independent runs. For  $\tilde{R} = 1$  the orientation of the dumbbell remains constant in time at  $\theta = 90^\circ$ , which is the initial orientation. For  $\tilde{R} > 1$  we scale the data by a fitted  $\tilde{\tau}$ , collapsing all the curves onto a master curve predicted by theory and represented here with a black dashed line. The inset shows the fitted relaxation time  $\tilde{\tau}$  for different  $\tilde{R}$ . In the range of  $\tilde{R}$  investigated,  $\tilde{\tau}$  is a monotonically decreasing function of  $\tilde{R}$ . (a) and (b) Results obtained at  $Pe = 480$  by implementing the model with constant  $s = 8.8 a_0$  and the model with  $s = R_1 + R_2$ , respectively. (c) and (d) Results obtained at  $Pe = 115$  by implementing the model with constant  $s = 8.8 a_0$  and the model with  $s = R_1 + R_2$ , respectively. The two models give similar results.

ure 1(c) where the dumbbell is composed of spheres with their surfaces at contact as we vary  $\tilde{R}$ . Hence the fluid is not allowed to flow in between them. The results are shown next to the first model in Figure 7(b) and (d). We observe that the two models give consistent results and the values of the  $\tilde{\tau}$  fall in the same range. Therefore we infer that the model of the dumbbell particle is robust within small variation in the design of the particle, and that the small gap between the spheres in the first model does not have any major consequence on the self-orientation phenomenon observed.

In order to assess the effect of side walls on the results, for selected state points we performed simulations in a wider channel, characterized by  $W \times H \times L_z = 200 \times 10 \times 400 a_0^3$ . We did not observe statistically significant deviations on the values of  $\tilde{\tau}$ .

## 4 Conclusions

In summary, we have performed numerical simulations to analyse the self-orientation process of an asymmetric dumbbell particle in

a shallow channel at different hydrodynamic regimes. We have implemented the MD+SRD simulation technique and have verified that this method is able to reproduce the correct velocity profile of the fluid flow.

Next, we have investigated the self-orientation process at different relative strengths of Brownian motion and for different particle shapes by varying  $Pe$  and  $\tilde{R}$ , respectively. We define three regimes of stability by analysing the amplitude of oscillations about the equilibrium position  $\theta = 0^\circ$ . For  $Pe \geq 400$  the alignment is strong for all  $\tilde{R}$ . As we lower the Péclet number,  $50 \leq Pe < 400$ , thermal fluctuations start to affect the self-orientation process first at large  $\tilde{R}$ , and progressively also at lower  $\tilde{R}$ . The self-alignment process is no longer possible for  $Pe < 50$  for any  $\tilde{R}$ .

On the basis of these results, we have computed the experimental conditions, as in flow rates and channel's dimensions, to achieve a certain level of alignment in asymmetric particles whose size ranges from tens of microns till fraction of microns. We expect this information will be of guidance for future experimental

work focusing on manipulating nanosized objects.

Moreover, we have computed the time dependence of the orientation angle  $\theta$ , and compared it with the theoretical prediction derived for the fully non-Brownian regime<sup>22</sup>. Our results are in remarkably good agreement with theory, even for intermediate Pe. We have fitted the analytical curves on our data set, where the fitting parameter is the reorientation relaxation time  $\bar{\tau}$ . We find that this parameter is a monotonically decreasing function of  $\bar{R}$ . We stress that this result is not in contradiction with recent work where the relaxation time shows a minimum for  $\bar{R} = 1.9$ <sup>23</sup>, since their model of dumbbell particle is fundamentally different from our model. In our model we increase  $\bar{R}$  by decreasing the radius of one sphere, leading to a particle composed of two beads for all  $\bar{R}$ . In their model the dumbbell is instead composed of two disks where the center-to-center distance is kept constant and the radius of one disk increases with increasing  $\bar{R}$ , thus eventually leading to a particle composed of only one disk for high  $\bar{R}$ .

This work has provided evidence that control over particle position and orientation is still possible at intermediate Péclet numbers, where diffusion becomes relevant in addition to convection. Our finding is relevant for scientific applications which rely on controlling dispersions in micron-sized devices at intermediate Pe. In fact, several devices are explicitly designed to operate in this regime<sup>42,43</sup> such as H-filters, which enable separation of species by exploiting the difference in diffusivity of the solute particles<sup>44</sup>. Since the diffusivity plays a key role in this process, it is clear that the range of applicability of these devices is confined to the low-to-intermediate Pe regime. Another fundamental aspect of this study reveals that the self-alignment still occurs at length scales of the order of the micron or fraction of micron. This finding is quite remarkable as there is no experimental evidence yet, to the best of our knowledge, which proves that hydrodynamic self-interaction can function at such small length scales. Therefore our work paves the way to new methods for particle sorting down to scales of fraction of microns by exploiting diffusivity, hydrodynamic self-interactions and particle shape to govern particle position and orientation.

## Conflicts of interest

There are no conflicts to declare.

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