# Supplementary Material for "Rotational diffusion of colloidal microspheres near flat walls"

Virginia Carrasco-Fadanelli,[1] Yushan Mao,[1] Tomoki Nakakomi,[2] Haonan Xu,[1] Jun Yamamoto,[2] Taiki Yanagishima,[2,*] and Ivo Buttinoni[1]

[1]*Institute of Experimental Physics of Condensed Matter, Heinrich-Heine University, Düsseldorf, Germany*

[2]*Department of Physics, Graduate School of Science, Kyoto University, Kyoto, 606-8224, Japan*

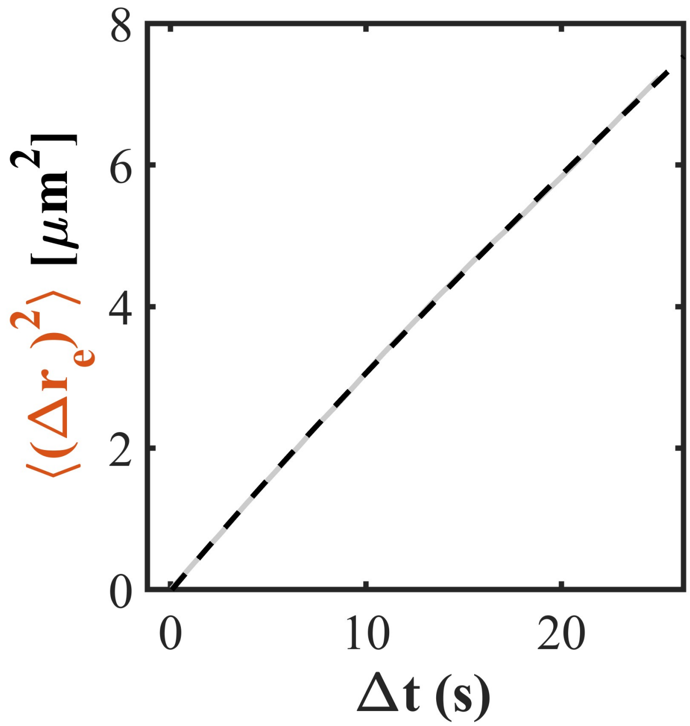


Fig. S 1. Mean-squared displacement of EC for OCULI particles away from walls. The dotted line is a fit using equation 3.

## MEAN-SQUARED DISPLACEMENT OF OFF-CENTER CORES

We consider the rotational diffusion of an OCULI particle, where the position of the eye $\mathbf{r_e}$ may be expressed relative to the position of the particle $\mathbf{r_p}$ as $\mathbf{r_e} = \mathbf{r_p} + r_{\text{rot}}\mathbf{u}$, where $\mathbf{u}$ is the orientation vector of the eye relative to the center, and $r_{\text{rot}}$ is the radius of rotation. The squared displacement of $\mathbf{r_e}$ over some lag time $\Delta t$ is then given by

$$\langle|\mathbf{r_e}(\Delta t) - \mathbf{r_e}(0)|^2\rangle = \langle|\mathbf{r_p}(\Delta t) - \mathbf{r_p}(0)|^2\rangle + r_{\text{rot}}^2\langle|\mathbf{u}(\Delta t) - \mathbf{u}(0)|^2\rangle + RT \tag{1}$$

where $RT$ represents all terms which include coupling between $\mathbf{r_p}$ and $\mathbf{u}$ i.e. translation-rotation coupling. Here, we assume that these terms are negligible. For a simple, single parameter characterization of the motion, we also assume that the rotational diffusion is isotropic with a diffusivity $D^r_{\text{eff}}$. It is known that the mean-squared displacement of the orientation vector is characterized by an exponential decay due to diffusive decorrelation and an asymptote due to the confined range of possible orientations, $\langle|\mathbf{u}(\Delta t) - \mathbf{u}(0)|^2\rangle = 2\left(1 - e^{-2D^r_{\text{eff}}\Delta t}\right)$ [1]. The translational mean-squared displacement term may also be expressed in terms of the translational diffusivity $D^t$ as $\langle|\mathbf{r_p}(t) - \mathbf{r_p}(t)|^2\rangle = 6D^t\Delta t$. Thus, the mean-squared displacement of the eye is given by

$$\langle|\mathbf{r_e}(\Delta t) - \mathbf{r_e}(0)|^2\rangle = 6D^t\Delta t + 2r_{\text{rot}}^2\left(1 - e^{-2D^r_{\text{eff}}\Delta t}\right) \tag{2}$$

However, the trajectory we measure is the $xy$-projection of this motion. By construction, the mean squared displacement should be equivalent when observed from all different directions. Thus, to account for reduced dimensionality, the expression is simply normalized by $\frac{2}{3}$. Finally, we note that the translational diffusivity term becomes $D^t_\parallel$ for particles sedimented onto a flat surface. The final expression becomes

$$\langle\Delta\mathbf{r_e}^2\rangle = 4D^t_\parallel\Delta t + \frac{4}{3}r_{\text{rot}}^2\left(1 - e^{-2D^r_{\text{eff}}\Delta t}\right). \tag{3}$$

## MEASURING ROTATIONAL DIFFUSIVITY IN BULK

It was shown that fluctuations in $z$ can have an adverse effect on measurements of $D^r_\parallel$. However, it is possible to extract $D^r_{\text{eff}}$ in any situation where rotational motion is diffusive. This includes a situation where particles are density matched to the solvent, allowing measurement in bulk. We realize this by dispersing OCULI particles with 2.6 $\mu$m diameter in bromocyclohexane (density 1.324 g/ml, viscosity 2.8 mPas [2]), which is roughly matched to the density of TPM particles (1.29 g/ml [3]). Four trajectories are recorded for particles at least 10 diameters away from the wall, 5000 frames each at 20 frames per second. A fit using equation 3 gives $D^t = 0.0624 \pm 0.0019$ $\mu$m$^2$s$^{-1}$ and $D^r_{\text{eff}} = 0.0326 \pm 0.0066$ s$^{-1}$, which are consistent with the Stokes-Einstein diffusivities expected at infinite dilution, $D^t_0 = 0.0599$ $\mu$m$^2$s$^{-1}$ and $D^r_0 = 0.0266$ s$^{-1}$. Since $z$ fluctuations do not impede the extraction of an effective rotational diffusivity, we stress that OCULI particles may be applied anywhere EC trajectories may be extracted.

## SUPPLEMENTARY VIDEO

EC and PC detection overlayed on a microscopy image with both bright field illumination and fluorescence excitation of the eye.

* yanagishima.taiki.8y@kyoto-u.ac.jp

[1] Albert P. Philipse, *Brownian Motion* (Springer International Publishing, 2018).

[2] P Ván, M Pavelka, and M Grmela, "Extra Mass Flux in Fluid Mechanics," J. Non-Equilib. Thermodyn. **42**, 133–151 (2017).

[3] Y Liu, T Yanagishima, A Curran, K V Edmond, S Sacanna, and R P A Dullens, "Colloidal Organosilica Spheres for Three-Dimensional Confocal Microscopy," Langmuir **35**, 7962–7969 (2019).