

Technical Report:

Experimental study of the nonlinear dynamics of Janus particles in complex fluids

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Abstract

Micromotors have been widely studied due to the nonequilibrium statistical mechanics observed at the initial regime. These microswimmers have wide applications in biophysics. The motion of the Janus micromotor at small time intervals, especially in and around the 'ballistic mode' remains an open problem. Moreover, the time dependence of active particles' mean squared displacement (MSD) constrained in polymers is little studied. Our goal is to study the diffusiophoresis of micromotors experimentally by setting randomly distributed Janus particles coated by Pt in polyethylene oxide (PEO) and H_2O_2 , and study its velocity, MSD, mean squared rotational angle (MSRA), the displacement probability distribution (DPD), etc., with regards to a time dependency. We hope to conclude a new paradigm of physical distribution at a short time diffusion stage, and explain it by mesoscale theory (Langevin Eq.).

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1 Introduction

1.1 Related works

Vicsek et al., 1995 [1]: Develop a model to show that velocity-driven particles result in a kinetic phase transition. Kulinskii et al., 2005 [2]: Developed a discrete algorithm for a continuum model based on Vicsek et al.’s work. ♦Howse et al., 2007 [4]: Experimental investigation: short time: lots of direct motion & velocity depends on fuel molecules concentration; long time: random walks & diffusion. Chang et al., 2007 [3]: Study the electro-osmotic flow propelled semiconductor devices. Gibbs et al., 2011 [6]: Study nanomotors with arms and found curvature, angular frequency, and radius of curvature of the trajectories change as a function of arm’s length. Angelani et al., 2011 [5]: Demonstrate that active baths are also capable of mediating effective interactions

between suspended bodies. Kümmel et al., 2013 [8]: Study asymmetric nanomotors (weird shaped) circular motion on a substrate and near channel boundaries, which results agree with Brownian dynamics for asymmetric self-propelled particles. ♦Zheng et al., 2013 [7]: Non-Gaussian statistics of spherical Janus particles in a long time. Buttinoni et al., 2013 [10]: Study the diffusiophoresis of Janus particles and found that the driving stabilizes small clusters at low densities & the suspension undergoes a phase separation into large clusters and a dilute gas phase at higher densities. Bialké et al., 2013 [9]: Report a dynamical instability leading to phase separation from numerical and analytical studies. Hagen et al., 2014 [12]: Demonstrate that a shape anisotropy alone is sufficient to induce gravitactic motion with either preferential upward or downward swimming. Zöttl and Stark, 2014 [11]: Simulate hydrodynamic flow fields with multiparticle collision dynamics. Wittmeier et al., 2015 [13]: Introduce Differential Dynamic Microscopy (DDM), and apply it to a single Janus particle to the rotational movement. ♦Gomez-Solano et al., 2016 [15]: Found an increase of up to 2 orders of magnitude of the rotational diffusion to the velocity of Janus particles. Bechinger et al., 2016 [14]: A comprehensive review on active particles. Molotilin et al., 2016 [16]: Multiscale simulation investigation of Janus particles in an electric field. Scholz et al., 2018 [17]: Experimentally demonstrate the significance of inertia on macroscopic self-propelled particles, and observe a distinct inertial delay between orientation and velocity of particles. Löwen, 2019 [18]: Extend the active Brownian motion model to active Langevin dynamics which include inertia to describe particles with inertia. Sahu et al., 2020 [19]: Indicate that dipolar force density produced by electric field interactions causes dielectric-forward (metal-forward) motion of the colloids. Shee et al., 2020 [20]: Compute Gaussian polymers and found that end-to-end distribution exhibits Gaussian behavior for short lengths, which changes to the form of semiflexible filaments at intermediate lengths, to finally go back to a Gaussian form for long contour lengths.

1.2 Anomalous diffusion

Anomalous diffusion is a diffusion process with a non-linear relationship between the mean squared displacement (MSD), $\langle r^2(\tau) \rangle$, and time. Anomalous diffusion has been

widely studied numerically and experimentally for active particles in non-constraint systems (i.e., water, H₂O₂) or in constraint systems (i.e., viscoelastic fluid, gel, polymers).

Havlin and Ben-Avraham, 2002 [21]: Diffusion in disordered systems: factual (linear stage) and random walks. Weigel et al., 2011 [24]: Diffusion in the plasma membrane of living cells: ergodic process resembles a fractal structure & nonergodic process can be modeled by a continuous-time random walk. ♦Bronstein et al., 2009 [22]: Telomeres diffusion in the nucleus of eukaryotic cells: short times the motion is subdiffusive with $\langle r^2 \rangle \sim t^\alpha$ and it changes to normal diffusion at longer times. Short time diffusion: reptation model. Sagi et al., 2011 [23]: The width of the cloud exhibits a power-law time dependence with an exponent that depends on the lattice depth. ♦Regner et al., 2013 [25]: Cytoskeletal transport along microtubules and diffusion in the cytosolic fraction exhibit anomalous (nonFickian) behavior and posses statistically distinct signatures; and continuous time random walk provides the best representation of diffusion. ♦Zheng et al., 2013 [7]: Three stages: simple Brownian motion at short times, superdiffusion at intermediate times, and finally diffusive behavior again at long times. Metzler et al., 2014 [26]: A comprehensive review on anomalous diffusion. Ramirez et al., 2018 [28]: Brownian dynamics simulation: three mechanisms of molecular diffusion of polymers at large length scales: hindered diffusion, walking diffusion, and molecular hopping. Krott et al., 2016 [27]: MD simulation of nanoparticles confined between two flat parallel plates: superdiffusive regime associated with a collective reorientation in a highly structured phase is observed. Benhamou, 2018 [29]: A comprehensive explanation on anomalous diffusion in Condensed Matter Physics. ♦Joo et al., 2020 [30]: Langevin dynamics simulation: the ABP cross-linker attains an active subdiffusion with the scaling $\langle \Delta r^2(t) \rangle \sim t^\alpha$ with $\alpha \gg 1/2$, through the viscoelastic feedback from the polymer. Sabri et al., 2020 [31]: Single-particle tracking experiments: particles stochastically switch between different mobility states, most likely due to transient associations with the cytoskeleton-shaken endoplasmic reticulum network. ♦Zheng et al., 2020 [32]: MSD & DPD: sub-diffusive behavior at short times and the non-Gaussianity at long times; The origin of the non-Gaussian anomaly at long times are elucidated as the non-ergodicity.

Woringer et al., 2020 [33]: A quick overview of the existing techniques used to analyze anomalous diffusion in cells.

1.3 Our approach

Inspired by Gomez-Solano et al.'s work [15], we are curious about the anomalous diffusion of Janus particles in viscoelastic fluids.

In Gomez-Solano et al.'s approach, they measure the MSRA $\langle \Delta\phi(t)^2 \rangle$ distribution and found an correlation with the effective rotational diffusion coefficient $D_r^{(Wi)}$, related with the Weissenberg number:

$$\langle \Delta\phi(t)^2 \rangle = 2D_r^{(Wi)}t$$

Such a relation is verified through experiments in their approach for long-time diffusion (up to 100s). For short-time diffusion, it is still an open case. Also, the time dependence of MSD is not discussed.

Our goal is to study the anomalous diffusion of Janus particles in viscoelastic fluid focusing on the **short time diffusion** through experiments to observe and conclude stages/modes for active particles' motion

2 Mathematical derivation

2.1 Brownian motion

We start the derivation from *the theory of forced Brownian diffusiophoresis*. Based on molecular thermodynamics, the relation of MSD $\langle \Delta r \rangle$ and diffusion coefficient D_t writes

$$\langle \Delta r \rangle^2 = 2nD_t t$$

where $n = 1, 2, 3$ are the dimensions. and the diffusion coefficient D_t takes the form

$$D_t = \frac{RT}{N_A} \frac{1}{3\pi\eta d}$$

where R is the Molar gas constant, equals $8.314472J/(mol \cdot K)$, T is the temperature, N_A is the Avogadro's constant, η is the viscosity of the fluids and d is the sphere's diameter.

We therefore elicit the *Stokes-Einstein relation* for diffusion coefficient, where D_t is the translational Brownian motion:

$$D_t = \frac{k_B T}{3\pi\eta d}$$

where k_B is the Boltzmann constant, equals R/N_A .

For polymers and nanoparticles, the thermal motion with the surrounding atoms also includes rotational Brownian motion, D_r . With the relations $D_r = 3D_t/d^2$ we have:

$$D_r = \frac{k_B T}{\pi\eta d^3}$$

Langevin, 1908: single particle's Brownian motion

$$m \frac{d^2 x}{dt^2} = -\lambda \frac{dx}{dt} + F(t)$$

where λ is Stokes drag, writes $\lambda = 3\pi\eta d$, $F(t)$ is the stochastic term, $\langle F(t) \rangle = 0$; is the total instantaneous force acting on the particle, writes

$$\langle F_i(t) F_j(t') \rangle = 2\lambda k_B T \delta_{ij} \delta(t - t')$$

Considering the external force $K(t)$, Langevin equation writes

$$m \frac{d^2 x}{dt^2} = -\lambda \frac{dx}{dt} + F(t) + K(t)$$

The normalized form of Langevin equation writes:

$$\frac{dx(t)}{dt} = v(t)$$

$$\frac{dv(t)}{dt} = -\frac{\lambda}{m} v(t) + \frac{1}{m} F(t) + \frac{K(t)}{m}$$

2.2 Effective diffusion coefficient

In diffusiophoresis situations, the diffusion coefficient is stated by effective diffusion coefficient D_{eff} , instead of D_t , taking the form

$$D_{eff} = \frac{\langle(\Delta r)^2\rangle}{2nt}$$

which can be also calculated through the half-height c_1 from Gaussian distribution:

$$D_{eff} = \frac{c_1^2}{4t}$$

For micromotors, the self propel equivalent diffusion coefficient can be derived from the Langevin equation:

$$D_{eff} = \frac{4R^2}{3\tau_r} + \frac{1}{4}V^2\tau_r + \frac{V^2\tau_r}{8t}(e^{-\frac{2t}{\tau_r}} - 1)$$

where τ_r is the rotational characteristic time for Janus particles, taking the form

$$\tau_r = \frac{\pi\eta d^3}{k_B T} = \frac{1}{D_r}$$

Therefore, D_{eff} writes

$$\begin{cases} D_{eff} = D_t + \frac{1}{4}V^2t, & t \gg \tau_r \\ D_{eff} = D_t + \frac{1}{4}V^2\tau_r, & t \ll \tau_r \end{cases}$$

♣ When $t \gg \tau_r$, D_{eff} linearly correlated with D_t , where the gradient is related with the self-propel velocity. When $t \ll \tau_r$, D_{eff} remains a constant, unrelated with observation time intervals.

3 Janus micromotor in polymers

3.1 Stages of MSD distribution

Recalling the Langevin equation

$$m \frac{d^2x}{dt^2} = -\lambda \frac{dx}{dt} + F(t) + K(t)$$

where for self-propelled particles, external force $K(t)$ taking the form $K = f\mathbf{U}$; for particles constrained in polymer networks, external force agrees $K = f(x)$.

Theoretically, for active particles constrained in cross-links, the following stages **might exists** within micromotors' motion:

- **Ballistic stage.** $\langle r^2 \rangle \sim t^2$ (*cannot be observed in exp.*)
- **Short time diffusion.** $\langle r^2 \rangle \sim D^s t$
- **Sub-diffusion.** $\langle r^2 \rangle \sim t^\alpha$, $\alpha < 1$
- **Long time diffusion.** $\langle r^2 \rangle \sim D^l t$
- **Self propelled.** $\langle r^2 \rangle \sim t^\alpha$, $\alpha > 1$
- **Brownian-like motion.** $\langle r^2 \rangle \sim t$

4 Experimental setup

4.1 Equipment

- **Optic Microscope & High Speed Camera:** Observe and collect the video shot of micromotors' movement in the solution.
- **Pt-coated Janus Particles:** SiO_2 (2000nm) from CUP.
- **PEO:** Polyethylene Oxide, PEO is a high-molecular-weight and non-ionic polymer. It is hydrophilic, linear and not cross-linked, and highly soluble in both aqueous and organic solvents. $M_w = 10^5$. PEO 0.1 %, 0.5 %, 1 %.
- **H₂O₂ Solution:** 30%.

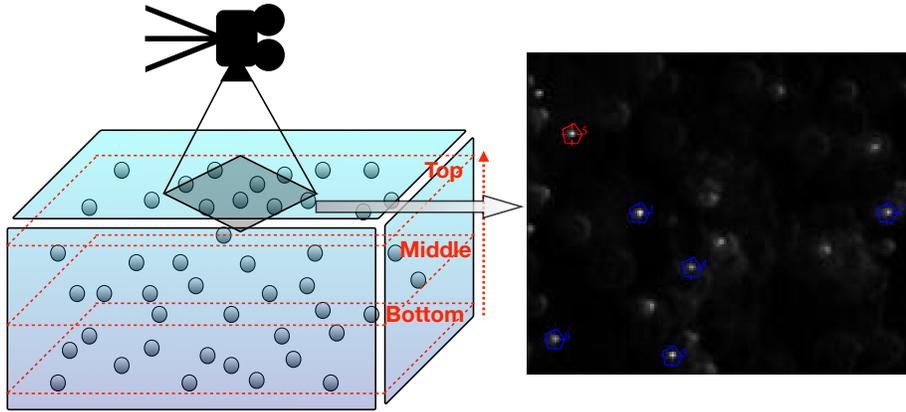


Figure 1: Schematic view of NP motion observations. The camera is placed on top to capture NP's motion at different altitudes (signified by Top, Middle, Bottom). **ImageJ** is utilized to preprocess the video for observation. **Video Spot Tracker** is used to capture different NPs, as illustrated on the right.

4.2 Software

- **ImageJ**: Record nanoparticles' rotational motion, measure displacements for MSRA $\langle \Delta\phi^2 \rangle$, DPRD, etc.
- **Video Spot Tracker**: Record nanoparticles' transnational motion, measure displacements for MSD $\langle \Delta r^2 \rangle$, DPD, etc.

5 Laboratory reports

5.1 Brownian motion of nanoparticles in water

Here we investigate the Brownian motion of nanoparticles (NP) distributed at different altitudes in water, marked as top, middle, and bottom. We first study the NPs' properties at the bottom by tracing six NP's motions. Then we study how NPs' Brownian motion behave at different altitudes by studying their Gaussianity, MSD, and related physical quantities.

5.1.1 NP at the bottom

We first analyze the NPs' motion at the bottom side. Six NPs are marked and followed for their coordinates' recordings. For each NP, 500 coordinates $(x_1, y_1), (x_2, y_2), \dots, (x_{500}, y_{500})$ was collected marking their motion in the full time scale.

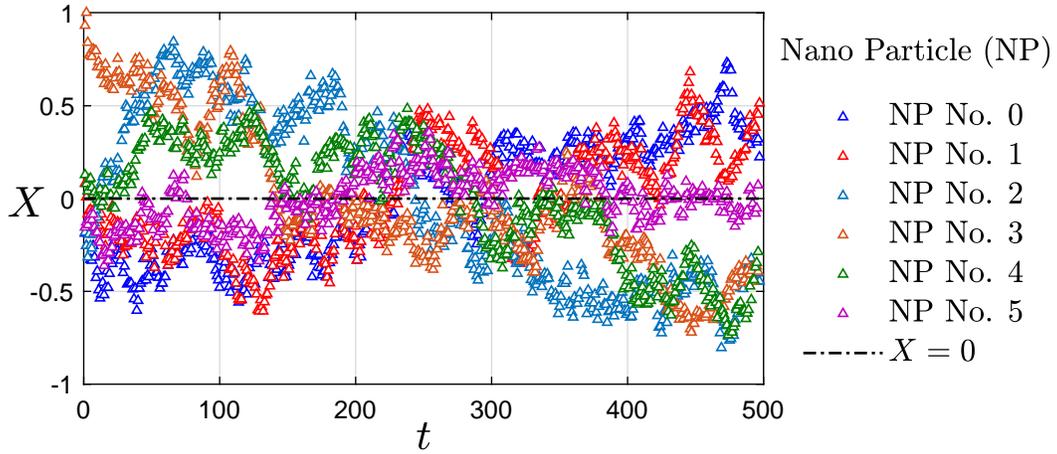


Figure 2: The displacements of the six NPs with regards to time. Six different NPs were signified by triangle dots of different colors. The black dotted line indicates zero displacements.

Figure 1 signifies our experimental process, where the motion of NPs are recorded at the prementioned different altitudes. Here we traced six NPs marked as No. 0, 1, ..., 5 as shown in the right subfigure in figure 1. The displacements of each NP are collected representing their Brownian motion in collected time. The probability distribution of each NP is measured as in figure 3, indicating non-Gaussianity of specific NP at the whole time scale. To analyze the probability of single NP, standard deviation σ and Kurtosis $\gamma_2 = \left(\frac{x-\bar{x}}{\sigma}\right)^4$ of the NPs are represented as in figure 4.

5.1.2 NP in full space domain

The double logarithmic plot of the MSD $\langle \Delta r^2 \rangle$ to time is shown in figure 5, where the relationships are linear, corresponds to the theory of NP self-diffusion in water. The probability distribution of all the six NPs recorded in the full-time scale is shown in figure 3, where Gaussianity is obeyed.

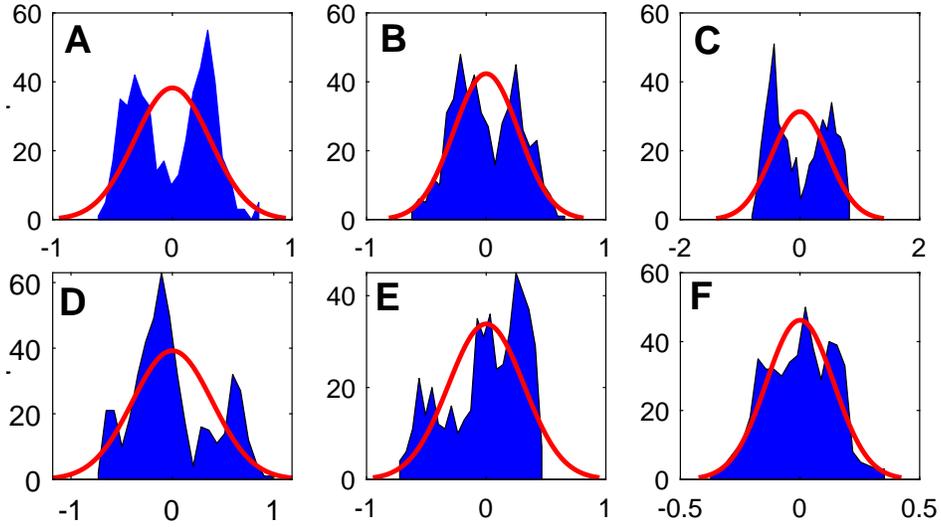


Figure 3: The probability distribution of the six NPs' displacements with regards to time. Note that the red solid line indicate the Gaussian distribution. **A** to **F** indicate NP from No. 0 to No. 5.

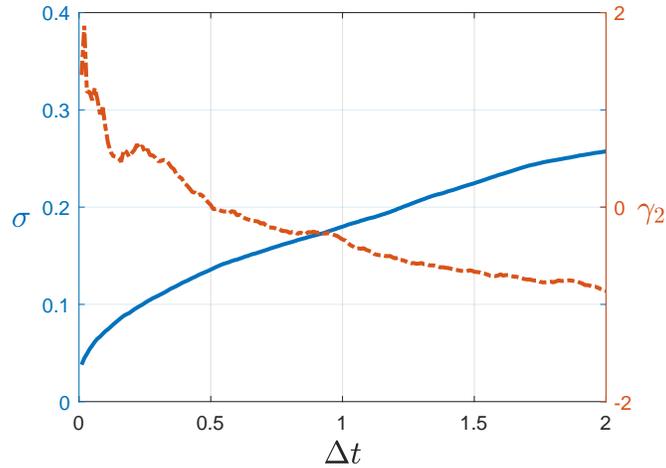


Figure 4: Error estimation of the probability distribution. The blue solid line indicates the standard deviation σ . The orange dotted line indicates the excess Kurtosis $\gamma_2 = \left(\frac{x-\bar{x}}{\sigma}\right)^4$ of the probability distribution.

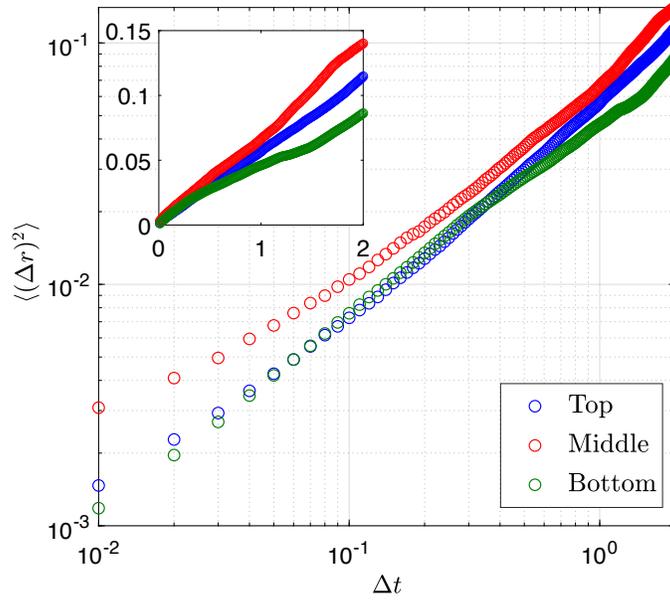


Figure 5: Double logarithmic plot of the experimental results for the MSD of NPs in water at different altitudes. The MSD is interpreted as a linear relation with time intervals Δt .

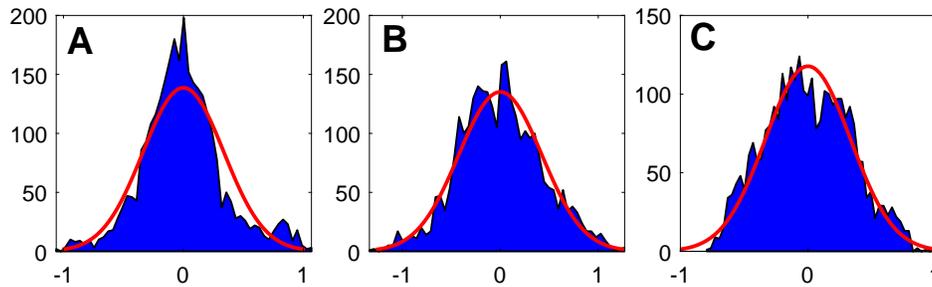


Figure 6: The probability distribution of NPs in the whole time scale in three different altitudes. Sub figure **A** indicates NPs in the top side, **B** indicates NPs in the middle side and **C** indicates NPs in the bottom side.

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