Orientational dynamics of a heated Janus particle

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Using large scale molecular dynamics simulations we study the orientational dynamics of a heated Janus particle which exhibits self-propulsion. The asymmetry in the microscopic interaction of the colloid with the solvent is implemented by choosing different wetting parameters for the two halves of the sphere. This choice leads to a different microscopic Kapitza resistance across the solid-fluid boundary of the two halves of the sphere, and consequently a gradient in temperature is created across the poles of the sphere. It is this self-created temperature gradient which leads to a self-propulsion along the direction of the symmetry axis. In this article, we look at the orientational dynamics of such a system, as well as the subsequent enhancement of the translational diffusivity of the heated Janus colloid at late times. The orientational correlation of the symmetry axis is measured from the simulation and provides a direct access to the rotational diffusion constant. The heating leads to an increase in the rotational diffusivity of the colloid. We quantify this increase in rotational diffusion $D_r$ against the temperature difference $\delta T \equiv T(R, 0) - T(R, \pi)$ across the poles of the Janus sphere as well as the average surface temperature difference $\Delta T \equiv T(R) - T(\infty)$ from the ambient fluid. Since the rotational diffusion is determined by the complete flow field in the solvent, we illustrate that comparing $D_r$ against $\delta T$ is misleading and is better quantified when compared against $\Delta T$. The later quantification results in a data collapse for different choices of the microscopic interaction. The average propulsion velocity is also measured for different choices of the wetting parameter. The directionality of self-propulsion changes depending on the microscopic interaction. We show that whenever the attractive interaction of the colloid with the solvent is switched off, the phoretic mobility changes sign. Further, the propulsion velocity is zero for heating below a certain threshold value. This is also corroborated by the probability distribution of the angle between the displacement vector $\Delta \vec{r}(t) \equiv \vec{r}(t) - \vec{r}(0)$ and the symmetry axis. Finally, we combine the measured propulsion velocity and the rotational diffusion time $\tau_r = 1/2D_r$ to estimate the enhancement in the long time diffusion coefficient of the particle.

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I. INTRODUCTION

Autonomous transport have gained a lot of attention from the scientific community. A variety of artificial micro and nano swimmers have been fabricated that exhibit different propulsion mechanisms. The recent impetus to study the single particle and collective motions of autonomous microswimmers is on one hand nourished by our interest to have a better understanding of the functioning of the living world down to the microscopic scale, and on the other hand by the diverse implications in technology, specifically the designing of nanomachines1–6. The key ingredient in any self-phoretic motion of a colloid is an asymmetry in the interaction with environment7–9, the most common example being the motion of a Janus particle in a thermal or a chemical gradient or both. Typically, for a Janus particle, the two surfaces have different chemical or thermal properties. For example, self-diffusiophoretic motion has been achieved by coating one half of a spherical particle with Platinum and immersing in a solvent containing Hydrogen Peroxide7. Similarly, self-thermophoretic motion is obtained by coating half of a Polystyrene sphere with a conducting material, such as Gold, and heating the composite particle in the focus of a laser4.

The theoretical formulation of estimating the net drift velocity of a microswimmer usually employs a hydrodynamic formulation where the slip layer is assumed to be small and the resultant slip velocity in the boundary layer is given by $\vec{u}_s = \mu_r \nabla \phi$, where $\mu_r$ is the spatially dependent phoretic mobility, $\vec{n}$ is the local normal to the surface and the choice of $\phi$ is dictated by the phoretic mechanism. For a diffusiophoretic self-propulsion $\phi$ is the concentration field while $\phi$ is the temperature field for thermophoretic self-propulsion. The drift velocity is then given by averaging the negative surface slip velocity $\vec{u}_s$ over the particle surface $S$. However, the hydrodynamic model, by its very definition coarse grains over the microscopic length scales and the complex dynamical processes at the microscopic level are often subsumed into the macroscopic transport coefficients such as the phoretic mobility. On the other hand, in experiments often these phenomena at the microscopic scale are not accessible. The gap is readily bridged by numerical simulations11–13.

In this article, using large scale molecular dynamics simulation, we study the self-thermophoresis of a Janus particle, with focus on the orientational dynamics of heated Janus colloid. Since the rectification of particle motion by its self-propulsion is limited by the rotational diffusion of its symmetry axis and effectively enhances the long time translational diffusion coefficient, a systematic investigation of the orientational dynamics needs to be done. While the translational degrees of freedom has been well studied, limited results exists for the dynamics of the orientational degrees of freedom11–14. We use a simple model system that was proposed earlier and is known to generate self-propulsion12–15. The asymmetry in the microscopic interaction is implemented through the modification of the...

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strength of the attractive term in the $12 - 6$ Lennard-Jones potential via the wetting parameter $c_{ab}$ (see Section II for more details). The model has several advantages – the attraction can be switched on and off by choosing a particular value of $c_{ab}$ and consequently the direction of propulsion can be changed. Additionally, the wetting parameter can also be made a continuous function of the polar angle $\theta$, effectively reducing the area of the model gold cap which is heated. In the present scenario we make the simplest choice of choosing constant values of $c_{ab}$ for the two different hemispheres of the spherical colloid. In our earlier work$^3$, while the model system was used to look at the temperature profile and the propulsion velocity generated as function of the heating of the colloid and to investigate the size of the slip layer around the heated Janus colloid, a systematic discussion on the orientational degrees of freedom and the subsequent enhancement of the long time translational diffusivity was not done. Hence, we focus on the orientational dynamics of a heated Janus particle, with the particular aim to look at the dependency of the rotational diffusion coefficient on the heating of the colloid and the microscopic wetting parameter. We summarize this section by pointing out that the main results of this work are contained in Figs. 4, 5 and 9.

The rest of the paper is organised as follows. In Section II we present our model system and the simulation details. The statics and dynamics of the symmetry axis is discussed in Section III. The propulsion velocity of the colloid and the enhancement in the translational diffusion coefficient at late times with increased heating of the colloid is presented in Section IV. Finally, a brief conclusion and outlook is presented in Section V.

II. MODEL SYSTEM AND SIMULATION DETAIL

Our simulation model consists of a nanoparticle immersed in a Lennard-Jones solvent. The microscopic interactions between the colloid and the solvent is given by the Lennard-Jones $12 - 6$ potential, $U_{ab}(r) = 4\epsilon \left[ (\sigma/r)^{12} - c_{ab} (\sigma/r)^6 \right]$, where $c_{ab}$ is the wetting parameter$^7$? . The nanoparticle is modelled as a spherical cluster of Lennard-Jones particle, bound together by the strong FENE potential $U(r) = -0.5kR_0^2 \ln (1 - (r/R_0)^2)$, with $k = 30\epsilon/\sigma$ and $R_0 = 1.5\sigma$. Further, the Janus particle is constructed from this spherical colloid by identifying an outer shell of atoms in the upper hemisphere of the colloid as a model Gold cap. The wetting parameter, introduced above, can take different values for the different types of pair interaction, namely $c_{ss}$ for the solvent-solvent, $c_{gs}$ for the model Gold cap-solvent, $c_{ps}$ for the model Polystyrene half-solvent, $c_{pg}$ for Polystyrene-Gold and $c_{gp}$ for Gold-Polystyrene. The broken symmetry between the two surfaces of the colloid is implemented by choosing different values for the wetting parameter in the interaction with the solvent, which effectively varies the minimum of the pair potential as $(2\sigma^6/c_{ab})^{1/6}$. Thus, for the value of $c_{ab} = 2$, the minimum distance between the centers of a particle in the colloid and the solvent is $\sigma$, whereas for $c_{ab} = 0$ the soft attractive part of the potential is completely lost. The value of $c_{ab}$ in the solvent-solvent interaction is kept constant at $c_{ss} = 1.0$. A variation in $c_{ss}$ is not important in the present discussion, since it only changes the phase diagram of the bulk solvent. Additionally, the wetting parameters for Gold-Polystyrene and Polystyrene-Gold interaction were fixed at $c_{pg} = c_{gp} = 1$. A typical simulation run consists of an equilibration phase in the NPT ensemble, with a Nöse–Hoover thermostat and barostat, at a temperature of $T_0 = 0.75\epsilon/k_B$ and a thermodynamic pressure of $p = 0.01\pi\sigma^3/\epsilon$. After the initial equilibration, for the rest of the simulation run, the system was evolved in a heating phase. During the heating phase, the global thermostat was switched off and the temperature $T_p$ of the gold cap was continuously controlled by a momentum conserving velocity rescaling procedure. Using a similar rescaling procedure, the fluid at the boundary of the simulation box was thermostated at the temperature $T_0$. For each nanoparticle temperature, at least three trajectories of $1.5 \times 10^7$ steps with $\delta t = 0.005\tau$ were simulated. All data was collected once the system reached a steady state. Throughout this paper, the value of a physical observable is obtained by averaging over these independent trajectories and the error bars denote the standard deviation of the mean. Further, mass, length, energy and time is measured in units of $m$, $\sigma$, $\epsilon$ and $\tau = \sqrt{\pi\epsilon/2\sigma^2}$.

A simple estimation of the heat diffusivity from the measured compressibility $\kappa_T$, and specific heat $c_p$ of the bulk solvent at the thermodynamic state of $(T_0, p)$ yields $D_T \equiv \kappa_T / (pc_p) \sim 2\tau^2/\tau$. On the other hand, the measured diffusivity of the Brownian particle at the same thermodynamic state point gives us $D \equiv k_B T / 6\pi m \eta \sim 0.003\pi^2/\tau$ ($R$ is the radius of the particle and $\eta$ is the viscosity of the solvent). The large value of the ratio $D_T/D$ supports the claim of time-scale separation between heat propagation and Brownian motion – heat diffuses much faster than the colloidal diffusion. As a consequence of the resulting NESS, the Brownian particle maintains a spa-
temporally varying and comoving temperature profile $T(t)$. At the microscopic level, there exists an interfacial thermal resistance (Kapitza resistance) across the solid-fluid boundary leading to a temperature discontinuity at the interface. This temperature discontinuity depends on the parameters of interaction between the solvent and colloid. In the molecular dynamics simulations, we exploit this microscopic phenomenon at the solid-fluid interface to create a temperature gradient $\delta T$ between the north-south poles of the spherical colloid. It is this gradient that generates an autonomous motion of the colloid.

III. ORIENTATIONAL DYNAMICS

In order to look at the orientational dynamics of the heated Janus particle, we recorded the unit vectors $\hat{x}$, $\hat{y}$, $\hat{z}$ in the body frame of the particle. The schematic illustration of this is shown in Fig. 1 (b). Throughout this article the vector $\hat{z}$ as denoted in the figure corresponds to the symmetry axis $\hat{n}$. At the beginning of the simulation, both the body and the lab frame coincide with each other. Accordingly, the unit vectors in the body frame were constructed at the beginning of the simulation by identifying the particles within the spherical cluster which were furthest from the center of colloid, along the three perpendicular directions. In the subsequent time steps, the unit vectors were computed by noting the positions of these particles relative to the center of mass of the colloid.

The hydrodynamic modeling of self-propulsion considers the motion to be force and torque free, and the symmetry axis performs a free diffusion on the surface of a sphere. In the lab frame, the symmetry axis is given by $\hat{z} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$, where $\theta$ and $\phi$ are polar and azimuth angle, respectively, that $\hat{n}(t)$ makes with the lab frame. The joint probability $p(\cos \theta, \cos \phi, t)$ follows the relation

$$p(\cos \theta, \cos \phi, t) = \sum_{l,m} e^{-\delta + (l+1)\frac{t}{\tau}} Y_{lm}(\cos \theta)$$  \hspace{1cm} \text{(1)}

In the steady state, with $t \to \infty$ only the $l = 0$ term survives and the stationary probability reads

$$p(\cos \theta, \cos \phi) = \frac{1}{4\pi}$$  \hspace{1cm} \text{(2)}

Integrating out $\phi$ from the joint probability $p(\cos \theta, \cos \phi)$ and transforming to the variable $\theta$ from $\cos \theta$ the probability $P(\theta)$ reads

$$P(\theta) = \frac{1}{2} \sin \theta.$$  \hspace{1cm} \text{(3)}

A similar procedure to evaluate $P(\phi)$ yields

$$P(\phi) = \frac{1}{2\pi}.$$  \hspace{1cm} \text{(4)}

To check whether the microscopic model confirm Eq. (3) and Eq. (4), we measured $\theta$ and $\phi$ from the trajectories of $\vec{z}(t)$ and constructed the probability density function (PDF) from independent configurations of the symmetry axis. The measured PDF, plotted in Fig. 2 agrees well with the theoretical prediction of Eq. (3) and Eq. (4).

To look at the dynamics of the symmetry axis, we measure the orientational correlation time $\tau_r$, from the simulations. An unbiased method to determine $\tau_r$ is to look into the correlation of the unit vectors in the body frame. For a rigid spherical object in an isothermal solvent, the orientation vector undergoes Brownian motion on the surface of sphere. Due to the symmetry of the sphere, the correlation of any orientation vector decays exponentially as:

$$C_\theta(t) \equiv \langle \vec{z}(t) \vec{z}(0) \rangle = e^{-2D_\theta t}.$$  \hspace{1cm} \text{(5)}

This provides us with a direct route to measure the rotational relaxation time $\tau_r = 1/2D_\theta$. To ensure that the numerical fit gives us the correct value of the rotational diffusion constant, we also numerically evaluated the function $Z_{\hat{n}}(t)$ defined as

$$Z_{\hat{n}}(t) = \frac{\dot{C}_\theta(t)}{C_\theta(t)}.$$  \hspace{1cm} \text{(6)}

FIG. 2. Distribution of the angle $\theta$ (figure (a)) and $\phi$ (figure (b)), the symmetry axis and its orthogonal projection makes with the $z$-axis and the $x$-axis of the lab frame. The solid lines in the figures are plots of the theoretical prediction Eq. (3) and Eq. (4). The particle temperature is $k_B T_p/\epsilon = 1.50$.

FIG. 3. The dynamics of the unit vectors $\hat{z}$ in the body frame is captured by their time correlation functions. Figure (a): Correlation of the symmetry axis $\hat{z}$ as a function of time for different heating of the colloid, $k_B T_p/\epsilon = 0.8$ (.), 1.30 (■), 1.50 (▲) and 2.00 (♦). The solid lines are fit to the data using Eq. (5). Figure (b): The numerical derivative defined by Eq. (6) with $\hat{n} = \hat{z}$. The dashed lines are the measured values of the rotational diffusion constant from a fit to the data using the functional form of Eq. (5). The colors indicate different temperature of the Janus particle as detailed in figure (a).
where \( \hat{\mathbf{n}} \) denote either of the unit vectors in the body frame. Using Eq. (5), the function \( Z_{\mathbf{n}}(t) \) at late time should saturate to \( D_r \) (see Fig. 3 (b)).

To further quantify the contribution of the rotational dynamics towards the long time diffusivity, we measured \( D_r \) for different heating’s of the Janus particle and different choices of the wetting parameter \( c_{gT} \). The rotational Brownian motion is a hydrodynamic phenomena which requires looking at the fluid flow generated in the whole system. Therefore, a quantification of \( D_r \) with heating of the colloid entails a subtlety of comparing against the local temperature difference \( \delta T \equiv T(R,0) - T(R,\pi) \) or \( \Delta T \equiv T(R) - T(\infty) \), the average temperature increment on the surface of the colloid above the ambient temperature \( T(\infty) \equiv T_0 \). The former can lead to a wrong interpretation of the data as illustrated in Fig. 4 (a) and (b). Even though the magnitudes are same for the complementary choices of the wetting parameters (such as \( c_{gT} = 2, c_{ps} = 1 \) and \( c_{gT} = 1, c_{ps} = 2 \)), \( D_r \) plotted against \( \delta T \) shows a counter-intuitive trend as expected from the behaviour of \( D_r \) as a function of \( T_p \) (see Fig. 4 (b)). Note that \( T_p \) is synonymous with \( \Delta T \). Had the rotational diffusion being a local phenomena, we would have expected that for increased values of \( \delta T \), the particle would rotate faster and the rotational diffusion would (since \( D_r \sim \tau_r^{-1} \)) also increase. Thus, we observe that for the choice of \( c_{gT} = 1, c_{ps} = 2 \) (filled squares in Fig. 5 (b)) the increase in \( \delta T \) is least, and therefore, we expect that the increase in rotational diffusion should be least. However, looking at Fig. 5 (a) we see that the increase in \( D_r \) is maximum (filled squares). A similar observation is also observed for the cases when \( c_{gT} = 2, c_{ps} = 0 \) and \( c_{gT} = 2, c_{ps} = 0 \). As a passing remark we note that \( D_r \) follows an Arrhenius behavior when plotted against \( \delta T \):

\[
D_r(\delta T) = D_r(0) e^{k_0 \delta T}.
\]

The value of \( k_0 \) varies for different choices of the wetting parameter, with \( k_0 \approx 6 \) is the maximum value for \( c_{gT} = 1 \) and \( c_{ps} = 2 \) and \( k_0 \approx 2 \) for \( c_{gT} = 0 \) and \( c_{ps} = 2 \) as well as for \( c_{gT} = 2 \) and \( c_{ps} = 0 \).

To properly quantify the effect of heating on rotational diffusion of the heated Janus particle we take a different approach. Since rotational diffusion of an isothermal as well as heated colloid \( ^\circ \) is known to be a hydrodynamic phenomena, we quantify the effect of heating on \( D_r \) by comparing it against \( \Delta T \). To this end, we look at the temperature profile in the solvent by averaging the kinetic energy in spherical shells of thickness 0.5\( \sigma \). The resulting radial temperature field is fitted to the solution of the Fourier’s heat equation with a temperature dependent thermal conductivity (8):

\[
T(r) = T_0 \left( 1 + \frac{\Delta T}{T_0} \right)^{R/r}.
\]

In order to take care of the periodic boundary condition imposed on the simulation box, the fit was used to determine the incremental temperature \( \Delta T \) and the ambient temperature \( T_0 \). The value of \( \Delta T \) and \( T_0 \) completely specifies the far away temperature field in the system and when \( D_r \) is plotted against the ratio \( \Delta T/T_0 \) we observe a data collapse for all the choices of the wetting parameters. To proceed further and quantify \( D_r \) in terms of \( \Delta T/T_0 \), we ignore the asymmetry in the temperature and the viscosity profile and use the framework of rotational hot Brownian motion \( ^\circ \). This approximation should be valid for small heating of the Janus particle, so that the non-linear effects due to the asymmetry does not appear. The rotational diffusion coefficient of the heated particle obeys the generalized Stokes-Einstein relation:

\[
D_r = k_BT_{HBM}^T/\tau_{HBM}^T.
\]
where $T^r_{\mathrm{HBM}}$ and $\xi_{\mathrm{HBM}}^r$ are the effective temperature and friction coefficient of the heated particle. Using fluctuating hydrodynamics, the effective parameters can be evaluated from the steady state temperature profile $T(r)$ and the viscosity profile $\eta(r)^{18,20}$. For convenience we reproduce the expressions for $T^r_{\mathrm{HBM}}$ and $\xi_{\mathrm{HBM}}^r$ that reads:

$$T^r_{\mathrm{HBM}} = \frac{\int_{R}^{\infty} T(r) \eta^{-1}(r) r^{-4} dr}{\int_{R}^{\infty} \eta^{-1}(r) r^{-4} dr}$$

(10)

and

$$(\xi_{\mathrm{HBM}}^r)^{-1} = \frac{3}{8 \pi} \int_{R}^{\infty} \frac{1}{\eta(r)r^4} dr.$$  

(11)

Under isothermal conditions, with $\Delta T = 0$, the effective temperature and the effective friction coefficient becomes $T^r_{\mathrm{HBM}} = T_0$ and $\xi_{\mathrm{HBM}}^r = 8 \pi \eta_0 R^2$, where $T_0$ is ambient fluid temperature and $\eta_0$ is the bulk viscosity of the solvent.

In a Lennard–Jones system the temperature dependence of the viscosity is given by

$$\log \left[ \frac{\eta(T)}{\eta_{\infty}} \right] = \frac{A}{T^4}.$$  

(12)

Using the radial temperature profile from Eq. (8), we transform the temperature dependence of the viscosity to a radial dependence, and use Eq. (10) and Eq. (11) to numerically calculate the rotational diffusion constant for different values of $\Delta T/T_0$. The numerical data is shown by the dashed line in Fig. 5, which agrees well for small values of $\Delta T/T_0$. A phenomenological fit using a quadratic polynomial

$$\frac{D_t(\Delta T)}{D_t(0)} \approx 1 + \frac{3}{2} \left( \frac{\Delta T}{T_0} \right) + \frac{5}{4} \left( \frac{\Delta T}{T_0} \right)^2$$

(13)

gives reasonable fit to the data for the whole range of $\Delta T/T_0$ investigated in the current work (the solid line in Fig. 5).

### IV. ENHANCEMENT IN TRANSLATIONAL DIFFUSIVITY

We next turn our attention to the enhancement of the late time diffusivity in the translation motion of the heated Janus particle. Ordinarily, for a spherical particle, the translational and rotational degrees of freedom are independent of each other, even in the scenario of symmetric heat absorption of the colloid. However, in self-phoretic motions, the different modes of motion become coupled, resulting in an enhanced diffusion of the colloid at late times. In the lab-frame, the Langevin equation in the overdamped limit for a self-propelled particle reads

$$\ddot{r} = V_p \ddot{z} + \xi$$

(14)

with $\langle \xi(t) \xi(t') \rangle = 2 D \delta(t - t') \delta_{ij}$ and $\langle \ddot{z}(t) \ddot{z}(t') \rangle = e^{-D_{ij} |t - t'|}$. The mean-square displacement (MSD) $\langle r^2(t) \rangle$ take the form,

$$\langle r^2(\Delta t) \rangle = 6 D \Delta t + 2 V_p^2 \tau r \left[ \frac{\Delta t}{\tau r} + e^{-2\Delta t/\tau r} - 1 \right].$$

(15)

FIG. 6. Time dependent diffusivity of a heated Janus colloid for temperatures $k_B T_p/\epsilon = 1.5$ (open circles) and $2.0$ (open squares). The dot-dashed lines corresponds to the translational diffusion coefficient $D_{\mathrm{HBM}}$ due to hot Brownian motion measured from the mean-square displacement in the $x - y$ plane. The dashed line corresponds to the value $D_{\mathrm{HBM}} + V_p^2 \tau r/3$ with values of $\tau_r$ and $V_p$ measured from the simulations.

where $V_p$ is the net propulsion velocity of the colloid, $D$ is the diffusion constant in absence of any broken symmetry and $\tau_r$ is inverse of twice the rotational diffusion constant. In a frame of reference rotating with the colloid, the motions along and perpendicular to the direction of propulsion are decoupled. Without loss of generality, we assume that the $z$-axis of the rotating frame is oriented along this direction (this also corresponds to the symmetry axis of the capped particle), and the MSD is given by

$$\langle \dot{x}^2(\Delta t) \rangle \equiv \langle \dot{y}^2(\Delta t) \rangle = 2D \Delta t,$$

$$\langle \ddot{x}^2(t) \rangle = 2D \Delta t + V_p^2 \Delta t^2.$$  

(16)

At late times, the MSD in the lab frame from Eq. (14) shows an increased diffusivity $D_{\mathrm{eff}}$ given by

$$D_{\mathrm{eff}} = D_{\mathrm{HBM}} + \frac{V_p^2 \tau_r}{3} = D_{\mathrm{HBM}}(1 + \chi).$$

(17)

with $\chi = V_p^2 \tau_r/3 D_{\mathrm{HBM}}$. The first term in Eq. (17) corresponds to the enhanced diffusivity of the heated particle due to its hot Brownian motion$^{8,18}$ while the second term has two competing physical mechanisms - an increase in the net propulsion velocity with heating and a decrease in orientational correlation time with heating.

As a first check we wanted to validate Eq. (17) from the measured time dependent diffusivity of the heated Janus particle. This validation is shown in Fig. 6, where we compare the long time diffusion coefficient with the predicted value in Eq. (17) and find excellent agreement of the predicted values with the measured diffusion coefficient.

The propulsion velocity is directly measured from the lab-frame particle velocity and projecting it in the body frame every time step. $^3$ To quantify the propulsion velocity $V_p$ with the heating of the colloid, we choose to do it against both $\delta T$ as well as $\Delta T$, separately. However, in order to make
We still choose to use $\delta$ for different combinations of the wetting parameters: $c_{gs} = 2, c_{ps} = 1$ (filled circles in figure (a)), $c_{gs} = 2, c_{ps} = 0$ (filled squares in figure (a)), $c_{gs} = 1, c_{ps} = 2$ (empty circles in figure (b)) and $c_{gs} = 0, c_{ps} = 2$ (empty circles in figure (b)). The solid lines are linear fit to the data, whereas the dashed lines denote the value $V_p = 0$ clearly indicating that for small heating there is no appreciable propulsion velocity. The shaded region in figure (a) indicate the non-linear regime.

a consistent estimate of the enhancement factor in the late time translational diffusion coefficient we use the later quantification against $\Delta T/T_0$.

It should be noted that since the hydrodynamic modelling of self-phoresis is a boundary value problem, this quantification of $V_p$ against $\Delta T/T_0$ is sufficient. We still choose to use $\delta T$ primarily to show that the phoretic mobility changes sign whenever the attractive interaction in either of the hemispheres is switched off.

The measured propulsion velocities reveal that irrespective of the choice of $c_{gs}$, there always exists a threshold in heating below which there no appreciable propulsion of the Janus particle (see Fig. 7) and the motion is purely diffusive. For higher heating’s of the colloid, a net propulsion in the direction of the symmetry axis emerges. This is also corroborated by the measured time dependent diffusion coefficient.\[\]

To explore this further, we look closely at the trajectory of the particle and calculate the angle $\alpha$ between the displacement vector $\Delta \mathbf{r}(t) \equiv \mathbf{r}(t) - \mathbf{r}(0)$ and the symmetry axis $\mathbf{z}(0)$ for values of $t$ which are less than the rotational relaxation time of the particle. In the absence of a directed motion, the rotational symmetry of the system is still preserved and therefore in the body frame the unit vector $\mathbf{r} = \frac{\Delta \mathbf{r}}{\Delta \mathbf{r}}$ rotates uniformly on a unit sphere. Consequently, the angle between the displacement vector $\Delta \mathbf{r}$ and the symmetry axis would follow a probability distribution given by Eq. (3). Although, we do not show this, it is indeed observed from the simulations, with the measured probability distribution of $\alpha$ following Eq. (3). When a directed motion emerges for higher heating of the colloid, the rotational symmetry is broken and the displacement vector would be oriented either towards or opposite to the symmetry axis $\mathbf{z}$, depending on the sign of the phoretic mobility. Accordingly, for a positive phoretic mobility the motion of the particle is along the symmetry axis when $\delta T < 0$ and opposite to the symmetry axis when $\delta T > 0$. Similarly, for a negative phoretic mobility the motion of the particle is along the symmetry axis when $\delta T > 0$ and opposite when $\delta T < 0$. We summarise these in the following:

\[
\begin{align*}
\mu > 0 & \quad \delta T > 0 \quad \text{propulsion opposite $\mathbf{z}$} \\
\mu < 0 & \quad \delta T < 0 \quad \text{propulsion along $\mathbf{z}$} \\
\mu > 0 & \quad \delta T > 0 \quad \text{propulsion along $\mathbf{z}$} \\
\mu < 0 & \quad \delta T < 0 \quad \text{propulsion opposite $\mathbf{z}$}
\end{align*}
\]

Since the directionality depends on the sign of the phoretic mobility, we looked at the distribution of the angle $\alpha$ for different choices of the wetting parameters, the particular cases with $c_{gs} = 2, c_{ps} = 1$ and $c_{gs} = 2, c_{ps} = 0$ are illustrated in Fig. 8. In the former scenario, the displacements at large times happen opposite to the symmetry axis, whereas when the attractive interaction is switched off the displacements happen along the direction of the symmetry axis. Although not shown in the plot, we observe a similar behavior when $c_{gs} = 1, c_{ps} = 2$ and $c_{gs} = 0, c_{ps} = 2$. We therefore conclude that in presence of an attractive interaction the average phoretic mobility $\mu$ is positive and becomes negative whenever one surface has a repulsive interaction. This dependence on the microscopic interaction raises the interesting fact that for a particular choice of the wetting parameters would make phoretic mobility zero and consequently, a dynamic switching of the wetting parameters in the experiments can result in a dynamical switching on/off of the transport, leaving hot Brownian transport unaffected.

Beyond the threshold value in heating, $V_p$ increases linearly in accordance with linear response. Additionally, we also observed that a non-linear regime in the propulsion velocity is achieved beyond an upper cutoff whenever the combination of the wetting parameter is such that the two halves of the Janus particle interacts with the solvent either strongly or weakly. In contrast, whenever either surface has a purely repulsive interaction, the propulsion velocity increases linearly throughout the range of heating that has been investigated.
Finally, we are in position to look at the term $V_p^2 \tau$ which contributes to the long time diffusivity $D_{HM}$. Since the effective translational diffusivity is determined by the complete flow field in the fluid, we choose to compare the augmenting term against $\Delta T / T_0$. A plot of the term $V_p^2 \tau$ against $\Delta T / T_0$ for different choices of the wetting parameters is shown in Fig. 9 (a). The enhanced translational diffusion coefficient at late times can reach almost 4 times the value of $D_{HM}$, the value in absence of self-propulsion. Comparing Fig. 9 with that of Fig. 7, we observe that whenever the propulsion is in the linear response regime, which happens when the attractive interaction with the solvent is switched off, the term $\tau V_p^2$ and therefore the enhancement factor approaches a saturation value for larger heating of the particle, indicating that $V_p$ does not increase sufficiently as compared to the decrease of $\tau$. On the other hand, if the propulsion velocity of the Janus sphere exhibits a non-linear dependence (for the case when $c_{gs} = 2, c_{ps} = 1$ and vice versa) on $\Delta T / T_0$, we do not observe any saturation in $\tau V_p^2$.

In order to have a better insight into Fig. 9 (a), in particular, whether $\chi$ monotonically increases with $\Delta T / T_0$, we look at the functional dependence of $V_p, \tau$, and $D_{HM}$ on $\Delta T / T_0$:

$$V_p = \tilde{\mu}(\Delta T / T_0)f(\Delta T / T_0), \quad D_{HM} = D_0g(\Delta T / T_0)$$

and

$$\tau = D_0h(\Delta T / T_0).$$

(19)

$D_0$ and $D_0$ are the translational and rotational diffusion constant of the colloid in the isothermal solvent. The functional forms of $g(x)$ and $h(x)$ follow from the theory of hot Brownian motion, whereas $f(x)$ follows from the measured propulsion velocity of the heated Janus colloid:

$$f(x) = (1 + c_1 x), \quad g(x) \approx 1 + c_2 x$$

and

$$h(x) \approx 1 + c_4 x.$$  

(20)

The coefficients $c_1, c_2$ can be exactly determined from the hydrodynamic theory of hot Brownian motion and depend on the microscopic interactions of the solvent particles. On the other hand the coefficient $c_1$ which quantifies the non-linear term in the propulsion velocity depends on the microscopic interaction parameters between the solvent and the colloid (see Fig. 7). Rewriting the term $\chi \equiv V_p^2 \tau / 3 DD_{HM}$ as

$$\chi \equiv \frac{V_p^2 \tau / 3 DD_{HM}}{\frac{\mu_e^2 x^2 f^2(x)}{6 D_0 D_0 g^{(3)}(x) h^{(3)}}},$$

(21)

with $x = \Delta T / T_0$. From Eq. (21) it becomes evident that a plot of $V_p^2 \tau / 3 \mu_e^2 D$ would exhibit a data collapse for different choices $c_{gs}$ whenever the non-linear increase in the propulsion velocity is not dominant. This happens when the heating of the colloid is small and in this regime $\chi \sim (\Delta T / T_0)^2$. This is indeed observed in the simulations (see Fig. 9 (b)). For all the choices of the wetting parameters that we have investigated, there is an initial data collapse and the initial increase in the $\chi$ is quadratic in $\Delta T / T_0$. However, for the choice of $c_{gs} = 2, c_{ps} = 0$ and $c_{gs} = 0, c_{ps} = 2$, the propulsion velocity increases linearly throughout the range of heating that we investigated ($c_1 = 0$) and consequently with increased heating $\chi \sim \Delta T / T_0$ and approaches a constant value when the linear terms in $g(x)$ and $h(x)$ becomes relevant (the dashed line in Fig. 9 (b)). On the other hand, for the choice of $c_{gs} = 2, c_{ps} = 0$ and $c_{gs} = 0, c_{ps} = 2$, after the initial quadratic increase, there is a small regime when the enhancement factor $\chi$ shows a cross over to a linear increase in $\Delta T / T_0$ but eventually increases again as $(\Delta T / T_0)^2$ when the linear term in $f(x)$ starts to dominate. Although not investigated in the current work, we note that from Eq. (21), $\mu_e \sim R^{-1}, D_0 D_0 - R^4$ and $\chi \sim R^2$.

V. CONCLUSION

In conclusion, we have presented a simple microscopic model system that can be used to investigate self-thermophoresis of a Janus particle. The microscopic interfacial resistance across the solid-liquid boundary is exploited to produce a self-created gradient across the poles of the sphere. It is this self-created temperature gradient which leads to a self-propulsion along the direction of the symmetry axis. The rotational diffusion constant is extracted from the time correlation of the symmetry axis $(\delta \theta(t) \tilde{\theta}(0))$ for different heating’s of the colloid, as well as for different choices of the wetting parameter. We quantify the measured rotational diffusion $D_0$ against the temperature difference $\delta T$ across the poles of the Janus sphere as well as the average surface temperature difference $\Delta T$ from the ambient fluid. Since the rotational diffusion is determined by the complete flow field in the solvent, we illustrate that comparing $D_0$ against $\delta T$ is misleading and is better quantified when compared against $\Delta T$ that results in a data collapse for different choices of the microscopic interaction. The average propulsion velocity is also measured for different choices of the wetting parameter and the directionality of motion changes depending on the microscopic interaction. We observe two important feature in the average propulsion velocity – first, for the choice of repulsive interaction the phoretic mobility changes sign and therefore, the direction of propulsion also reverses. This is also corroborated by the probability distribution of the angle between the displacement vector $\Delta \theta(t) \equiv \theta(t) - \theta(0)$ and the symmetry axis.
z(0). And second, when either half of the sphere has a repulsive interaction, the propulsion velocity remains in the linear response regime even for higher heating of the colloid. On the other hand, whenever the interaction of the solvent with the colloid has an attractive term, we observe a non-linear dependence of $V_p$ with the temperature difference $\delta T$. This indicates that repulsive interaction suppresses the phoretic mobility of the particle, and can be exploited in designing artificial microswimmers. Further, the propulsion velocity exhibits a threshold in heating below which there is no appreciable self-propulsion. Finally, we combine the measured propulsion velocity and the rotational diffusion time $\tau_r = 1/2D_r$ to estimate the enhancement in the long time diffusion coefficient of the particle $D_{eff} = D_{HBM}(1 + V^2_p \tau_r / 3D_{HBM})$.

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VII. REFERENCES

1. M. N. Popescu, S. Dietrich, M. Tasinkevych, and J. Ralston, The European Physical Journal E 31, 351–367 (2010).
2. M. N. Popescu, M. Tasinkevych, and S. Dietrich, EPL (Europhysics Letters) 95, 28004 (2011).
3. R. Golestanian, T. B. Liverpool, and A. Ajdari, New Journal of Physics 9, 126–126 (2007).
4. H.-R. Jiang, N. Yoshinaga, and M. Sano, Physical Review Letters 105 (2010), 10.1103/PhysRevLett.105.268302.
5. P. A. E. Schoen, J. H. Walther, S. Arcidiacono, D. Poulidakos, and P. Koumoutsakos,Nano Letters 6, 1910–1917 (2006).
6. S. Chen, Journal of Colloid and Interface Science 224, 63–75 (2000).
7. J. Howse, R. Jones, A. Ryan, T. Gough, R. Vafabakhsh, and R. Golestanian, Physical Review Letters 99, 048102 (2007).
8. D. Chakraborty, M. V. Gnann, D. Rings, J. Glaser, F. Otto, F. Cichos, and K. Kroy, EPL (Europhysics Letters) 96, 60009 (2011).
9. D. Rings, M. Selmk, F. Cichos, and K. Kroy, Soft Matter 7, 3441 (2011).
10. S. Merabia, P. Keblinski, L. Joly, L. Lewis, and J.-L. Barrat, Physical Review E 79 (2009), 10.1103/PhysRevE.79.021404.
11. M. Yang, A. Wysocki, and M. Ripoll, Soft Matter 10, 6208 (2014).
12. M. Yang and M. Ripoll, Soft Matter 9, 4661–4671 (2013).
13. M. Yang and M. Ripoll, Physical Review E 84, 061401 (2011).
14. T. Bickel, G. Zecua, and A. Würger, Physical Review E - Statistical, Non-linear, and Soft Matter Physics 89, 1–5 (2014).
15. M. Vladkov and J.-L. Barrat, Nano Letters 6, 1224–1228 (2006).
16. J.-L. Barrat and F. Chiurutini, Molecular Physics 101, 1605–1610 (2003).
17. B. ten Hagen, S. van Teeffelen, and H. Löwen, Journal of Physics: Condensed Matter 23, 194119 (2011).
18. D. Rings, D. Chakraborty, and K. Kroy, New Journal of Physics 14, 053012 (2012).
19. S. Auschra, G. Falasco, D. Chakraborty, R. Pfaller, and K. Kroy, “Coarse graining nonisothermal active colloids,” (2017), unpublished Work.
20. N. V. Brilliantov, V. P. Denisov, and P. L. Krapivsky, Physica A: Statistical Mechanics and its Applications 175, 293–304 (1991).

21. D. Lüsebrink, Colloidal Suspensions in Temperature Gradients with Mesoscopic Simulations, Ph.D. thesis, Universität zu Köln (2011).