

Orientation of Janus Particles under thermal fields: the role of internal mass anisotropy

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Janus particles (JPs) are a special kind of colloids that incorporate two hemispheres with distinct physical properties. These particles feature a complex phase behavior and they can be propelled with light by heating them anisotropically when one of the hemispheres is metallic. It has been shown that JPs can be oriented by a homogeneous thermal field. We show using multiscale simulations and theory that the internal mass gradient of the JPs can enhance and even reverse the relative orientation of the particle with the thermal field. This effect is due to a coupling of the internal anisotropy of the particle with the heat flux. Our results help to rationalize previous experimental observations and open a route to control the behavior of JPs by exploiting the synergy of particle-fluid interactions and particle internal mass composition.

I. INTRODUCTION

Janus particles (JPs) are colloids made of two or more components with different properties. The first synthetic Janus particle consisted of amphiphilic glass spheres featuring hydrophilic and hydrophobic hemispheres¹. Since then, a range of particles with different compositions have been synthesized, including colloids coated with metallic patches². Metals are of particular interest in thermal applications, since the metallic patch can be heated with light, by exploiting the plasmon resonance effect. This idea was realized by Jiang *et al.*³, who measured the temperature distribution and temperature slip around a JP, and demonstrated that the anisotropic temperature distribution leads to the self-propulsion of the colloids. Following these works the investigation of JP suspensions have gained much popularity in the area of active matter, and as models to investigate exotic phase behavior⁴ and test non-equilibrium transport theories employed in the description of biological microswimmers⁵. A good understanding of the physical behaviour of JPs under non-equilibrium conditions will contribute to their implementation in practical applications⁶, by exploiting their amphiphilic and self-propulsion properties.

In this work we investigate the behaviour of JPs in a homogeneous thermal field. Recently, it was predicted that JPs orient in a thermal field⁷. Experimental work using polystyrene beads with one hemisphere coated with gold confirmed the existence of a preferred orientation, with the gold side pointing to the heat source⁸. This orientation effect was interpreted in terms of an effective slip velocity associated to a varying thermal gradient around the particle surface.

Due to the anisotropic composition of JPs, the colloids feature internal mass gradients, with the center of mass of the colloid shifted from its center of geometry. We showed recently, using non-equilibrium thermodynamics theory and simulations, that such internal mass gradients lead to thermophoretic

torques, and the orientation of axially symmetric particles in a thermal field⁹⁻¹¹. Hence, our hypothesis is that coupling effects associated to internal degrees of freedom contribute to the orientation of JPs too, and might contribute significantly to determine the preferred orientation of the JPs. We explore this hypothesis in the present Letter using both atomistic and mesoscopic simulations supported by a theoretical approach that describes accurately the orientation of JP in terms of their internal mass distribution.

II. SIMULATION METHODS

We show in Fig. 1a the atomistic simulation setup, consisting of two JPs suspended in an atomic fluid. The particles are located in the geometric center of the two subvolumes around the middle of the simulation box. The simulation cell is fully periodic, and it incorporates two thermostatting regions that define hot and cold boundaries (see coloured regions, red-hot and blue-cold in Figure 1(a), and see reference⁹ for an extended discussion). In the stationary state the thermostats generate a stationary heat flux and temperature profile. The center of mass of the colloids was tethered to the geometric center of each compartment using a harmonic potential. The solvent is modelled atomistically, setting its density to that of a typical liquid, $\rho^* = (N/V)\sigma^3 = 1.0$, where N is the number of solvent particles, $V = L_x \times L_y \times L_z$ is the volume of the simulation cell, L_ξ the box length in direction ξ , and σ_s is the diameter of the solvent particles. The JPs were modelled as amorphous rigid bodies composed of atoms of diameter $\sigma_p = \sigma_s$. The mass of the solvent, and the atoms in the JP were $m_s = m_p = 1.0$. Solvent-solvent (ss) and solvent-particle (sp) interactions were modelled using the Lennard-Jones potential, truncated and shifted at $r_c = 2.5\sigma$. The solvent-solvent and solvent-particle interaction strength was set to $\epsilon_{ss}/k_B T = 1$. In all the simulations reported here $\nabla T T^{-1} R < 1$, hence within the linear response regime.

To investigate the mesoscopic length-scales associated to very large colloid to solvent diameter ratios, we performed mesoscopic simulations using the Stochastic Rotation Dynamics (SRD) algorithm¹², implemented in LAMMPS^{13,14}.

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Specific details on the treatment of the SRD fluid are presented in the SI. The number of SRD particles per cell was set to $n = 5$, with reduced mass density $\rho_m = 1.0$ and mean free path $\lambda = 0.1a_0$, where $a_0 = 1.0$ is the lateral size of the SRD cells. The mesoscopic JPs were modelled as core-shell particles of radius R with mass density equal to that of the SRD fluid. The coupling between the SRD fluid and JPs is achieved through stochastic collisions with the shell, following the method reported in reference¹⁰ to simulate thermal fields. Further details of the SRD-JPs model are given in the Supplementary Information.

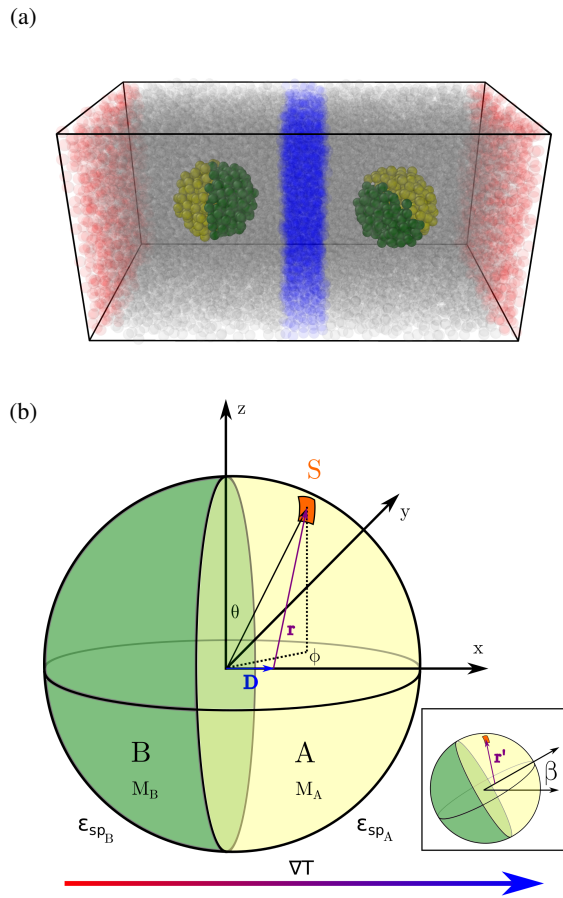


FIG. 1. (a) Snapshot of the simulation box employed in our work. Red and blue regions indicate the position of the hot and cold thermostats, respectively. The fluid particles are represented as translucent grey spheres and the JP with yellow and green spheres. (b) Sketch of the Janus particle, showing the polar (θ) and azimuthal (ϕ) angles, as well as the definition of the mass dipole \mathbf{D} , which appears in the figure fully aligned along the direction (x) of the thermal gradient, ∇T . The vector \mathbf{r} connects the centre of mass of the particle to the surface element, S , highlighted in orange. The inset shows the rotation of the JP by an angle β . The orientation vector with respect to the heat flux, \mathbf{J}_q , is given by $\cos\beta = \mathbf{u}_c \cdot \mathbf{u}_{J_q}$, with $\mathbf{u}_c = (\mathbf{r}_{cm_A} - \mathbf{r}_{cm_B}) / |\mathbf{r}_{cm_A} - \mathbf{r}_{cm_B}|$, and \mathbf{r}_{cm_A} and \mathbf{r}_{cm_B} being the vectors defining the centre of mass of the hemispheres A and B.

III. THERMOPHORETIC TORQUE AND ORIENTATION OF THE JP

To understand the role of the internal mass anisotropy on the thermophoretic torque, we simulated JPs with different mass distributions, $\gamma = m_A/m_B \geq 1$, where m_α is the total mass of hemisphere α . We kept the solvent-particle interactions for both hemispheres identical ($\epsilon_{sp_A} = \epsilon_{sp_B} = 1.0$). The simulations show that the JPs orient in a thermal field (see Figure 3), and the orientation increases with the mass anisotropy (γ) and particle size (R). We note that the orientation of JPs has been interpreted before in terms of the changes in the slip velocity around the nanoparticle, which arise from different hemisphere-fluid interactions⁷. Our simulations were performed using the same interaction strength for both hemispheres, hence the effect reported here is due to the mass anisotropy. We also performed simulations using our mesoscopic SRD model. This model features a very similar dependence, with the particle orientation increasing both with γ and R , showing that the mass anisotropy induced torque operates in a wide range of length scales. We find in both cases, atomistic and mesoscopic, that the the JP orients with the heavier side pointing preferentially towards the hot region.

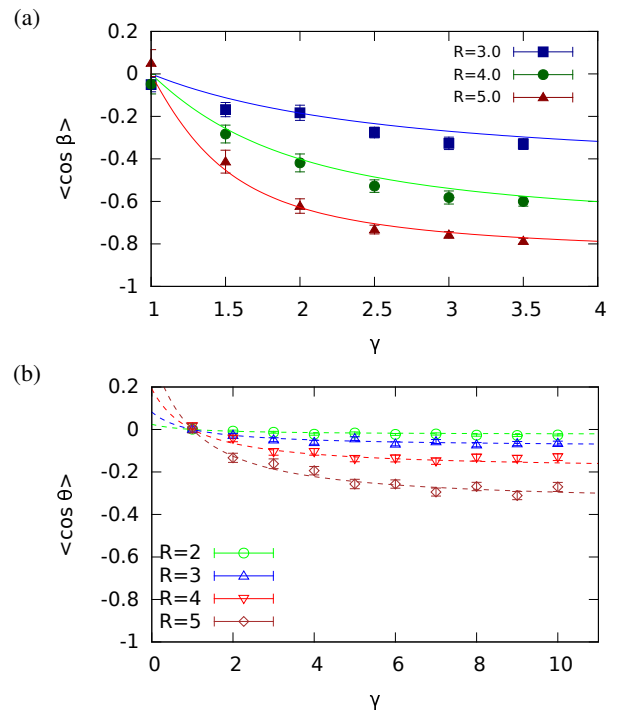


FIG. 2. (a) Average orientation of atomistic JP as a function of the mass ratio, γ and particle size, R . All the data were obtained with $\nabla T = 0.08$, the average temperature of the colloid centre of mass $T = 2.5$ and particle-fluid interaction $\epsilon_{sp_A} = \epsilon_{sp_B} = 1.0$. (b) Average orientation of the mesoscopic SRD JP as a function of γ . The data correspond to $\nabla T = 0.12$ and average temperature $T = 2.5$. The solid lines in panels (a) and (b) represent the theoretical predictions from Eqs. (5) and (6).

We discuss in the following a theoretical model that explains the dependence of the orientation with the mass

anisotropy, γ , and the particle size R . It is well known that thermal fields induce thermophoretic forces in colloidal particles, with the colloids drifting towards hot or cold regions. The thermophoretic force, \mathbf{f}_T is defined by^{15,16}:

$$\mathbf{f}_s - \mathbf{f}_T = s_T k_B T \nabla T \quad (1)$$

where s_T is the Soret coefficient, T the temperature of the colloid, ∇T is the temperature gradient and \mathbf{f}_s the thermophoretic force on the solvent. $s_T > 0$ indicates that the JP drifts towards the cold region. We assume that the thermophoretic torque leading to the orientation reported above, arises from the different thermophoretic forces acting on the two hemispheres of the JP, when the particle is suspended in the thermal field. To implement the model, we computed the \mathbf{f}_T of homogeneous particles varying their size and mass. Due to the large colloid/solvent mass ratio, $\mathbf{f}_s \ll \mathbf{f}_T$, and \mathbf{f}_T is the dominant term defining s_T , \mathbf{f}_s being $\sim k_B \nabla T$.

Our simulation of atomistic and mesoscopic particles show a quadratic dependence of the Soret coefficient with the colloid radius (see Figure 2 in the SI), revealing a linear dependence of s_T with the surface area of the colloid, which can be modelled via a Soret coefficient defined as,

$$s_T = 4\pi R^2 \zeta, \quad (2)$$

where ζ is a new parameter that quantifies the Soret coefficient per unit area. We note experiments have reported both quadratic, (R^2) and linear (R) dependencies of the Soret coefficient with the particle radius^{17,18}. While the Soret coefficient in our simulated models changes with R^2 , the theoretical treatment presented here could be extended to consider a linear dependence, by including this in the equations for the torque (see equations below).

We use now the expression for s_T (equation 2) obtained above to derive an equation describing the orientation of the JP as a function of mass anisotropy and size. We include the internal mass contribution using the concept of *mass dipole*⁹, D , defined as the distance between the centre of mass and the geometric centre of the JP. At the atomistic scale $D_a = \frac{3R}{8} \left(\frac{\gamma-1}{\gamma+1} \right)$, and at the mesoscopic scale $D_m = \frac{3R}{16} \left(\frac{\gamma-1}{\gamma+1} \right)$ (see the SI for a derivation of these equations), where $\gamma = m_A/m_B$, quantifies again the mass anisotropy of the JP.

The mass dipole is used to define the position of the surface element on the JP (see Fig. 1) relative to the particle center of mass, $\mathbf{r} = (R \sin \theta \cos \phi - D, R \sin \theta \sin \phi, R \cos \theta)$. The contribution of an element of area of the JP, located at position $\mathbf{r} = (R \sin \theta \cos \phi - D, R \sin \theta \sin \phi, R \cos \theta)$ (see Fig. 1b), to the thermophoretic force in the direction of the temperature gradient is $d\mathbf{f}_{\nabla T} = -\zeta_\alpha k_B T \nabla T dA$, where $dA = R^2 \sin \theta d\theta d\phi$ is the area of the element in spherical coordinates. The thermophoretic torque in the direction perpendicular to the thermal gradient is (see SI for details on the derivation),

$$d\tau = -\zeta k_B T \nabla T (R^3 \sin^2 \theta \cos \phi \sin \beta - DR^2 \sin \theta \sin \beta + R^3 \sin \theta \cos \theta \cos \beta) d\theta d\phi \quad (3)$$

where β defines the angle that the mass dipole of the JP makes with the thermal gradient (see Figure 1b). The torque of the JP follows from the integration of Eq. (3) over θ and ϕ ,

$$\tau = 4\pi R^2 \zeta D k_B T \nabla T \sin \beta \quad (4)$$

Integration of the torque with respect to β gives the free energy $F = -\int_0^\beta \tau_\perp d\beta'$, and the corresponding probability p for the JP to adopt a specific orientation in the thermal field is $p = \exp(-F/k_B T)$, with $p(\beta, \kappa) = \exp(\kappa \cos \beta) / (\pi I_0(\kappa))^{10}$. I_0 is the modified Bessel function of the first kind, and κ is the von Mises distribution parameter, given by:

$$\kappa = -4\pi R^2 \zeta D \nabla T \quad (5)$$

Using p above we get the average orientation of the JP,

$$\langle \cos \beta \rangle = \coth \kappa - \frac{1}{\kappa}, \quad (6)$$

i.e. the Langevin function. A similar equation has been obtained before to define the polarization of active JPs⁷, by considering the viscous stress acting along the surface of the JP, which arises in that case from differences in the mobility of the fluid at both hemispheres. However, our equation (6) is defined "only" by the presence of an inhomogeneous mass distribution inside the colloid. Other effects, e.g., connected to the distortion of temperature gradients around the particles could be included, to take into account non-isothermal surfaces, which would lead to a non-zero slip velocity proportional to the gradient (see e.g. refs.^{7,8}).

We have tested the accuracy of our equation (6) against the simulation data (see Figures 2(a) and (b)). At high mass ratios γ the orientation saturates, while it still depends on R . This behavior is connected to the mass dipole, D , which indeed saturates at large γ , while it depends linearly on the particle radius. The agreement between the orientations obtained with theory and simulations is excellent, both for the small and large colloidal regimes.

IV. COUPLING OF MASS AND FLUID-PARTICLE INTERACTION EFFECTS

We showed above that internal mass anisotropy induces thermophoretic torques in a JP. Previous studies demonstrated that differences in fluid-particle interactions do also induce thermal orientation in JPs⁷, hence we investigate in the following the coupling of these two effects, in order to quantify their importance in determining the orientation of JPs in the thermal field. All the simulations discussed below were performed with the atomistic model and a JP of radius $R = 5.0$. To assess this synergistic effects between mass dipole and fluid-particle interactions, we changed systematically both the mass and solvent-particle interactions of hemisphere A, keeping the properties of hemisphere B constant. We set $\epsilon_{spA} = 0.4$

or 2.2, while $\epsilon_{spB} = 1.0$. The mass of hemisphere A was varied in the range $1-10 m_B$.

In the absence of mass anisotropy the hemisphere in the JP with the strongest solvent-fluid interaction is expected to orient preferentially towards the cold region. This notion follows from the general dependence of Soret coefficient with the particle-fluid interaction strength (see e.g. ¹⁹). Indeed, for mass homogeneous particles, $\gamma = 1$ and a weak interaction between one of the hemispheres and the solvent ($\epsilon_{spA} = 0.4$), we find that $\langle \cos \beta \rangle < 0$ (see Figure 3), indicating that the hemisphere interacting more strongly with the solvent orients preferentially towards the cold region. This tendency can be reversed easily by increasing the interaction of the other hemisphere with the solvent, which eventually leads to a reversal of the orientation, such that $\langle \cos \beta \rangle > 0$ (see $\epsilon_{spA} = 2.2$ in Figure 3). Interestingly, we find that the mass anisotropy, γ , can enhance the orientation of the particle in a given direction, but also it can reverse it, as shown by the change of sign of $\langle \cos \beta \rangle < 0$ with γ (see Figure 3). We therefore conclude that both, particle-solvent interactions and mass anisotropy, influence the orientation of the JPs.

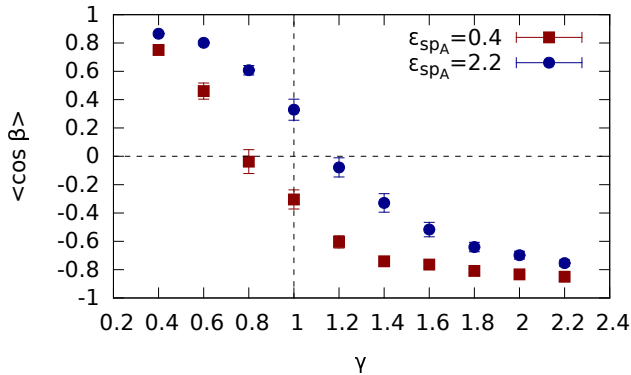


FIG. 3. Average orientation of a Janus colloid of size $R = 5.0$ with both mass and interaction anisotropy, under a temperature gradient $\nabla T = 0.12$ and temperature $T = 2.5$.

The result presented above might help to rationalize experimental results reported before (see ref.⁸). These experiments were performed with micrometer size JPs, synthesized by coating half of a $1 \mu\text{m}$ polystyrene (PS) sphere with a thin layer (50 nm) of gold, which is adsorbed on a thin layer of chromium (5 nm) directly attached to the PS⁸. The metallic layer will interact strongly with a polar fluid, such as water. From the analysis of typical density profiles for water-gold and water-alkane interfaces (taken the alkane as a proxy of the polymer part of the particle), we estimated the ratio of energies for the gold-water / polymer-water interactions, ~ 3.5 (see SI). In the experiments these particles are shown to orient with the metallic hemisphere pointing towards the hot region. This is the opposite orientation to what is expected in terms of particle-fluid interactions (see above), which would reorient the JP such that the stronger interacting surface points towards the cold region. Using the experimental data for the composition of the JP studied in ref.⁸ and a particle radius of $0.5 \mu\text{m}$, we estimate a mass ratio of $\gamma \sim 7$. We performed additional

simulations spanning different mass ratios, including $\gamma \sim 7$, and targeting an interaction ratio of the order of the one one estimated above, $\epsilon_{spA}/\epsilon_{spB} = 10/0.4$ (see Figure 4 in the SI). Our model predicts that the such particle would orient with the stronger interacting hemisphere pointing towards the hot region, hence in agreement with the experiments (see Figure 4). In addition to help rationalizing the experimental results our analysis shows that the interaction and mass anisotropy effects play a key role in determining the “polarization” of the JP under thermal fields.

V. CONCLUSIONS

In summary we have performed a multiscale simulation study of Janus Particles (JPs). We demonstrated that the coupling of the mass anisotropy, a property intrinsic to the composition of JPs, and the heat flux in a homogeneous thermal field, induces the orientation of the JP. We have modelled the mass dependence using a theoretical approach that relies on the calculation of the Soret coefficient per unit area. This theory accurately describes the orientation of the JPs with their mass anisotropy.

The strong coupling of the mass anisotropy of the JPs and the thermal fields is reproduced in both, atomistic and mesoscopic models, hence supporting our view that mass-induced thermophoretic torques operate in a wide range of solvent/colloid size ratios. The synergy of JP-solvent interactions and mass dipole couplings provides new opportunities to manipulate JPs using thermophoretic “tweezers” and possibly a route to control the structure of JPs assemblies by induces assembly in specific orientations. The effect discussed in this work might influence the behavior of colloids with internal mass anisotropy, under the influence of two external fields, e.g. magnetic and thermal fields, since it would add an additional torque contribution to the forces experienced by the colloids and potentially affect transport properties. Further experimental work to address this problem would be of great interest.

SUPPLEMENTARY MATERIAL

See Supplementary Material for additional details on geometrical considerations and simulation methods.

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AIP PUBLISHING DATA SHARING POLICY

The data that supports the findings of this study are available within the article and its supplementary material.

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