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Active Brownian motion tunable by light

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Abstract

Active Brownian particles are capable of taking up energy from their environment and converting it into directed motion; examples range from chemotactic cells and bacteria to artificial micro-swimmers. We have recently demonstrated that Janus particles, i.e. gold-capped colloidal spheres, suspended in a critical binary liquid mixture perform active Brownian motion when illuminated by light. In this paper, we investigate in more detail their swimming mechanism, leading to active Brownian motion. We show that the illumination-borne heating induces a local asymmetric demixing of the binary mixture, generating a spatial chemical concentration gradient which is responsible for the particle’s self-diffusiophoretic motion. We study this effect as a function of the functionalization of the gold cap, the particle size and the illumination intensity: the functionalization determines what component of the binary mixture is preferentially adsorbed at the cap and the swimming direction (towards or away from the cap); the particle size determines the rotational diffusion and, therefore, the random reorientation of the particle; and the intensity tunes the strength of the heating and, therefore, of the motion. Finally, we harness this dependence of the swimming strength on the illumination intensity to investigate the behavior of a micro-swimmer in a spatial light gradient, where its swimming properties are space-dependent.

(Some figures may appear in colour only in the online journal)
Illumination-borne heating generates a local spatial chemical concentration gradient which is eventually responsible for the particle’s self-diffusiophoretic motion. We study this effect as a function of the functionalization of the gold cap, the particle size and the illumination intensity. We finally study a situation where the self-diffusiophoretic motion is spatially inhomogeneous by using an illumination gradient.

The micro-swimmers used in our experiments consist of silica spheres (SiO$_2$, Microparticles GmbH, Germany) with different radii ($R = 0.5, 1, 2.13$ µm). One side of these spheres is coated by thermal evaporation with a thin adhesion layer of chromium (2 nm) and, subsequently, with a thicker layer of gold (20 nm). In order to control which component of the mixture is preferentially adsorbed at the gold surface, we render it either hydrophilic or hydrophobic by chemical functionalization with thiols terminated with either polar (11-mercapto-undecanoic acid) or nonpolar (1-octadecanethiol) end groups. These Janus particles are then diluted in a critical binary mixture of water and 2,6-lutidine [30]. In figure 1(b) a schematic phase diagram of the mixture is shown. At the critical composition ($T = 0.286$ mass fraction of lutidine) and below the lower critical temperature ($T_c = 307$ K) the mixture is homogeneous, as shown by the bright-field picture in inset (i) of figure 1(b). Increasing the temperature above $T_c$, the mixture separates via spinodal decomposition as shown in inset (ii) of figure 1(b). The bicontinuous wormlike structure is typical of the spinodal decomposition and has been observed not only in binary fluids [31, 32], but also during the phase separation of metallic alloys [33], glass alloy systems and polymeric blends with high molecular weight [34, 35].

The temperature of the critical suspension is kept a fraction of a degree below the critical point with a flow thermostat (point A in figure 1(b)). The whole sample ($170 \times 130$ µm) is then illuminated with green light at $\lambda = 532$ nm near the plasmonic absorption peak of gold [36]. Due to light absorption, the gold caps are heated above $T_c$; the temperature at the silica side does not change because silica does not absorb green light. Thus, the illumination triggers the heating of the caps and, subsequently, the local demixing of the critical mixture. In our experiments,

Figure 1. Active Brownian micro-swimmers in a critical binary mixture. (a) Schematic explaining the self-propulsion mechanism: a Janus particle is illuminated and the cap is heated above $T_c$ inducing a local demixing that eventually propels the particle. (b) A schematic phase diagram for water–2,6-lutidine. The insets are bright-field microscopy pictures of the mixed (i) and the demixed (ii) phase at the critical concentration.
homogeneous illumination is obtained by rapidly scanning a highly defocused (spot radius $\approx 30 \mu m$) laser beam over the entire area of the sample using an acousto-optical deflector. The light intensity is kept lower than $10 \mu W \mu m^{-2}$ in order to rule out optical forces, which are typically relevant only for $I$ at least an order of magnitude larger.

In order to better understand the heating process induced by the illumination, we have numerically estimated the temperature increase $\Delta T$ for an incident light intensity comparable with the experimental values. Heat is generated only in the cap because of the absorption associated to the imaginary component of the dielectric constant of gold [36], and then diffuses in the surrounding medium, i.e. silica sphere and water–2,6-lutidine, according to the Poisson heat equation. We followed in more detail the approach outlined in [37]: by applying the green dyadic method [38], we could estimate the electric field $E$ inside the gold cap under uniform plane-wave illumination; then we derived the heat power $Q$ generated at the cap, whose temperature is assumed to be uniform due to the high heat conductivity of the gold; finally, we calculated how $Q$ diffuses in the surrounding medium using the Poisson heat equation and the heat conductivity of silica and water–2,6-lutidine. We note that $\Delta T$ is independent of the base temperature of the mixture. Figure 2 shows the results of the simulation of $\Delta T$ in the equatorial plane of a Janus particle with $R = 0.5$ (figure 2(a)), 1 (figure 2(b)) and 2 $\mu m$ (figure 2(c)) illuminated with green (532 nm), linearly polarized light of $I = 1 \mu W \mu m^{-2}$; brighter colors correspond to a larger $\Delta T$. The particles, whose contours are indicated by the dashed lines, are oriented so that the caps points to the left. As the particle size increases, $\Delta T$ becomes larger, because of the larger dissipation at the gold cap. More interestingly, we notice that $\Delta R$ is strongly asymmetric for all three particle sizes and that a sharp temperature transition occurs at the edge between the capped and uncapped sides of the particle; this asymmetry is responsible for the localization of the demixing at the cap side, for the instauration of a chemical gradient across the particle and, eventually, for the micro-swimmer’s self-propulsion.

When the temperature locally increases above $T_c$, the binary mixture locally demixes and generates a demixed region around the Janus particle. In order to understand how this demixing fuels the particle’s directed motion, we need to visualize its size and shape. Therefore, we added a fluorescent dye (Rhodamine 6G), which preferentially dissolves in lutidine, to the mixture and mapped the resulting fluorescence intensity. In figure 3, we show the fluorescence intensity encoded in color, i.e. yellow (red) for high (low) fluorescence intensity. Figure 3(a) shows the concentration of lutidine around a Janus particle with a hydrophilic-functionalized cap. The cap is easily identified as the bright half-moon shape at the center of the picture. Upon illumination, the lutidine becomes depleted from the area near the cap (red, water-rich phase), while it accumulates at the silica side (yellow, lutidine-rich phase), which is hydrophobic (in comparison to the hydrophilic-functionalized cap), thus resulting in a concentration gradient around the particle. The particle moves within this gradient in the direction of the lutidine-rich phase as indicated by the black arrow. Figure 3(b) shows the lutidine concentration around a Janus particle with a hydrophobic cap. In this case, the lutidine-rich phase (yellow) accumulates at the cap, while the water-rich (red) phase gets depleted and accumulates at the silica side, the latter being more hydrophilic than the cap. Again, the particle moves in the resulting gradient towards the lutidine-rich phase (arrow). These measurements confirm self-diffusiophoresis as the driving mechanism for the observed active motion. In order to rule out other possible mechanisms of self-propulsion, in particular self-thermophoresis, we repeated these measurements in pure water; here, we did not observe any directed motion under illumination intensities comparable those used in our experiments.

After having investigated the driving mechanism, we studied the motion of such micro-swimmers by injecting a diluted suspension in a thin glass cell ($\approx 100 \mu m$ high). Owing to gravity, the particles sediment to the bottom of the sample cell and their motion is effectively constrained to two dimensions (for the illumination intensities considered in this work). We recorded movies at 7.5 frames s$^{-1}$ and employed digital video microscopy to track the particle trajectories at different illumination intensities. When the sample is kept at a temperature far from $T_c$, i.e. $\Delta T \gg 1 K$, the local illumination-induced heating is not sufficient to cross the spinodal line and, therefore, to induce a local demixing. On increasing the illumination intensity, the trajectories remain Brownian with a diffusion coefficient thus given by the Stokes–Einstein formula $D_{SE} = \frac{k_B T}{6 \pi \eta R}$, where $\eta$ is the binary fluid viscosity [30] and $k_B$ is the Boltzmann constant. When the base temperature of the sample is kept very close to $T_c$, i.e. $\Delta T \approx 0.1 K$, the local heating is strong enough to cross the spinodal line and, thus, to induce a local demixing and to propel the particle. For smaller particle sizes, due to the lower heat power, higher illumination intensities are required, in agreement with the results from the simulations presented in figure 2.

The resulting motion is characterized by a crossover from ballistic motion at short times to enhanced diffusion at longer times, the latter due to random changes in the swimming direction [24, 26, 39]. The corresponding average particle speed $v$ along the short-time ballistic runs, and the crossover time $\tau$ from the ballistic to the diffusive regime, can be estimated from the mean square displacement (MSD) [29]. Figure 4 shows the resulting values. The values of $v$ as a
Figure 3. Demixed regions around illuminated Janus particles. (a) Distribution of the lutidine-rich phase (yellow), labeled with a hydrophobic dye (Rhodamine 6G), around a Janus particle with a hydrophilic gold cap (bright half-moon shape) under illumination. (b) Same as (a) for a Janus particle with a hydrophobic gold cap. Since the size of the demixed regions depends on the illumination intensity, the latter is set significantly higher than in the other experiments we present (10 $\mu$W $\mu$m$^{-2}$) in order to better visualize the gradient.

Figure 4. (a) Velocity ($v$) of self-propelled Janus particles as a function of the illumination intensity. (b)–(d) Crossing time ($\tau$) for particles with radius $R = (b) 2.13$, (c) 1.0 and (d) 0.5 $\mu$m. The values of $\tau$ are shown in figures 4(b), (c) and (d) for $R = 2.13$, 1.0 and 0.5 $\mu$m, respectively. It is evident that smaller micro-swimmers tend to change direction much more frequently. Interestingly, the values of $\tau$ for a given particle size are almost independent of the illumination intensity. These fitted values of $\tau$ agree with $\tau = 1/D_t$ within the experimental error bars (figure 5), where

$$D_t = \frac{k_B T}{8\pi \eta R^3} \tag{1}$$

is the rotational diffusion of the particle. This suggests that the cap reorientation is mainly due to free rotational diffusion and remains rather unaffected by the propulsion mechanism. We note that this decoupling of rotational and translational motion largely simplifies corresponding numerical simulations of this system.

The possibility of tuning the active Brownian motion of the micro-swimmers can be employed in various contexts. For example, we have harnessed the dependence of the swimming strength on the illumination intensity to investigate the behavior of a micro-swimmer in a spatial light gradient, where its swimming properties are space-dependent; these conditions resemble the situation of bacteria moving inside a chemical gradient. Figure 6(a) shows the trajectory of a micro-swimmer moving inside a radial illumination gradient; the radial dependence of the intensity is shown in figure 6(b). The particle starts from the lower left corner, where, since...
there is almost no light, it undergoes standard Brownian motion. As soon as the particle randomly moves closer to the center, it starts to perform active Brownian motion with increasingly high \( v \) as it approaches the high-intensity center of the gradient; the radial dependence of \( v \) is plotted in figure 6(c). Furthermore, the trajectories become more directed and less rough as the active motion increases.

In conclusion, we have described a self-propulsion mechanism based on the local asymmetric demixing of a critical binary mixture around a microscopic Janus particle. The main advantage of this mechanism is that, since the required heating is very small (a fraction of a kelvin), the active Brownian motion can be easily tuned by a very weak illumination, which permits us to avoid optical forces acting on the highly asymmetric Janus particles. Furthermore, it is possible to control the active Brownian motion of the micro-swimmers both in space and in time by employing spatial and temporal illumination patterns.

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