Self-diffusiophoresis of Janus particles in near-critical mixtures

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We theoretically study the self-propulsion of a laser-heated Janus particle in a near critical water-lutidine mixture, and relate its velocity \(v_p\) and squirmer parameter \(\beta\) to the wetting properties of its two hemispheres. For non-ionic surface forces, the particle moves the active cap ahead, except at strong driving, where a more complex behavior occurs if one of the hemispheres attracts water and the other lutidine. Both \(v_p\) and \(\beta\) show non-monotonic dependencies on the heating power, and may even change sign. Including the drift of the counterions due to the composition gradient, we find that a charged cap with lutidine affinity drives the particle the cap ahead, and with water affinity in the opposite direction, in agreement with experimental findings.

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In recent years, artificial microswimmers without mechanical parts have been realized by Janus particles which move along the concentration or temperature gradients generated by their own chemical or thermal activity. Self-propulsion results in enhanced Brownian motion with a large effective diffusion coefficient \([1–5]\), dynamically generated electric fields and ion effects may contribute to the motion \([12, 13]\); in the case of ionic molecular solutes, self-propulsion results in enhanced Brownian motion \([14, 15]\). The underlying mechanisms have generally a strong diffusiophoretic component \([12, 13]\): in the case of ionic molecular solutes, self-generated electric fields and ion effects may contribute to the motion.

Diffusiophoresis was first rationalized by Derjaguin et al. \([16]\), when observing that wax particles dispersed in a non-uniform glucose solution, migrate toward lower sugar concentration. Because of its unfavorable interaction with wax \((u > 0)\), sugar is depleted in the boundary layer, the adsorption parameter \(\Gamma = \int_0^\infty dz z\left(e^{-u/k_B T} - 1\right)\) is negative, and the wax particle migrates to lower glucose content at the velocity \(v_p\)

\[
v_p = \frac{2k_B T}{3\eta} \Gamma \nabla n,
\]

where \(\eta\) is the solvent viscosity. For a molecular solute that is attracted by the surface, one has \(\Gamma > 0\) and the particle moves toward higher concentration.

There is no such simple rule for self-propelling Janus particles, where both the adsorption parameter and the concentration gradient vary along the particle surface, and where catalytic coating may result in a multicomponent boundary layer \([12, 18]\). A particularly intricate situation occurs for hot Janus particles in a near-critical water-lutidine mixture \([4]\), which migrate in a self-generated composition gradient. Though their motion is clearly related to the wetting properties of their active and passive surfaces \([7, 19, 20]\), there is at present no explanation for the sign and magnitude of the velocity.

In this Letter we study self-diffusiophoresis in such near-critical binary mixture \([4, 7, 19]\). The particle velocity \(v_p\) and the squirmer parameter \(\beta\) strongly depend on the ratio of the adsorption parameters on the two hemispheres, and of the fraction of the particle surface satisfying critical conditions. As a function of the heating power, both \(v_p\) and \(\beta\) show a non-monotonic behavior and may change sign in various instances. Finally, we find evidence that the motion of charged Janus particles depends on the solvation properties of their counterions.

The critical droplet. Fig. 1 illustrates an active Janus particle in a water-lutidine mixture at the critical water content \(\phi_C = 0.72\) and at a bulk temperature \(T_0\) which is slightly below the critical value \(T_C = 34.1\) °C. Illuminating the particle with a laser beam, raises the surface temperature above its critical value \(T_C\) and results in local demixing. Assuming a quadratic relation between the excess temperature and the local change of composition, \(T - T_C = C(\phi - \phi_C)^2\), one finds for the volume fraction of water

\[
\phi(r) - \phi_C = \pm \sqrt{\frac{T(r) - T_C}{C}},
\]

where \(r\) is the radius of the droplet, and the squirmer parameter \(\beta\) are plotted as a function of the cosine of the polar angle \(\epsilon = \cos \theta\). The ordinates are chosen such that the critical values coincide. The surface temperature takes the value \(T_m\) at midplane, its maximum \(\sqrt{2}T_m\) at \(c = 1\), and its minimum \(2 - \sqrt{2})T_m\) at \(c = -1\).

FIG. 1: Critical droplet \((\phi > \phi_C)\) surrounding a particle with hydrophilic surface coating on both the cap (red) and the uncapped hemisphere (white). The temperature profile (calculated from the thin-cap limit of Ref. \[21]\) and the order parameter \([15]\) are plotted as a function of the cosine of the polar angle \(\epsilon = \cos \theta\). The ordinates are chosen such that the critical values coincide. The surface temperature takes the value \(T_m\) at midplane, its maximum \(\sqrt{2}T_m\) at \(c = 1\), and its minimum \(2 - \sqrt{2})T_m\) at \(c = -1\).
where the two signs correspond to phases rich in water and lutidine, and where $C \approx 100{ \degree}C$ \cite{22}. This mean-field relation ceases to be valid at the critical point where composition fluctuations become long-range. The right panel shows the temperature and composition profiles along the particle’s midplane.

A more complex situation occurs for a particle with a hydrophobic cap, as illustrated in Fig. 2. If the critical temperature is reached on both hemispheres, the critical droplet splits in lutidine-rich and water-rich compartments, with the phase boundary attached at the particle’s midplane \cite{23}. This separation is possible since the interface tension between the spinodal phases, $\gamma < 10^{-4}$ N/m for $T < 36{ \degree}C$ \cite{22}, is much smaller than the particle’s surface energy. For the strong-heating case shown in the lower panel, the critical volume is almost spherical with radius $a(T_m - T_0)/(T_C - T_0)$, much larger than the particle radius $a$. Experiments cover the whole range from a small demixing area to a large critical droplet of tens of microns \cite{19}.

**Slip velocity.** Contrary to the critical droplet of composition $\phi$, the boundary layer is not in a quiescent state, but shows a non-uniform pressure and a steady diffusion current. Inserting the latter in Stokes’ equation, one finds the effective slip velocity \cite{24},

$$v_s = -\frac{k_BT}{\bar{v}\eta} \frac{d\phi}{dx},$$

with the adsorption parameter

$$\Gamma = \int_0^\infty dz \frac{e^{-\psi_w} - e^{-\psi_l}}{\phi e^{-\psi_w} + (1 - \phi)e^{-\psi_l}}.$$  \hspace{1cm} (4)

The effective potentials $\psi_l = \bar{v}_l u_l/k_BT$ are given in units of the thermal energy; they depend on the excess energy densities of water and lutidine, $\bar{u}_w$ and $\bar{u}_l$, which vanish well beyond the interaction range $\lambda$, and on the factor accounting for the molecular volumes $\bar{v}_l^{-1} = \phi_l \bar{v}_l^{-1} + (1 - \phi_l)\bar{v}_w^{-1}$ \cite{24}. Derjaguin’s adsorption factor is readily obtained in the dilute limit $\phi \to 0$ when identifying $u = k_BT(\psi_w - \psi_l)$. Note that that the slip velocity $v_s$ does not depend on the parallel force component $\partial \psi_{\perp}$, but on the composition gradient only \cite{25}.

For an order-of-magnitude estimate, it is convenient to explicit the adsorption parameter for a square well potential of width $\lambda$ and prefactor $\bar{\psi}$, where the integral in \cite{22} gives $2\lambda^2$ with $\bar{\psi} \to \bar{\psi}$ in the second factor. A strongly hydrophobic surface repels water and attracts lutidine ($\psi_w > \psi_l$), such that $\Gamma < 0$, whereas a hydrophilic surface is characterized by $\Gamma > 0$. With typical parameters \cite{19} we find $\Gamma \sim 10^{-21}$ m$^2$ and, supposing an interaction length $\lambda$ of a few Å, we deduce $\bar{\psi} \sim 10^{-2}$. Then the adsorption parameter $\Gamma = \frac{1}{2}\lambda^2(\bar{\psi}_l - \bar{\psi}_w)$ takes a constant value on each hemisphere, which is denoted $\Gamma_{\text{cap}}$ on the cap and $\Gamma_{\text{unc}}$ on the remainder.

**Self-propulsion.** The particle velocity is obtained by averaging the slip velocity over the surface, $v_{p} = -\langle v_s \rangle$ \cite{20}. For an axisymmetric particle one finds

$$v_p = \frac{k_BT}{2\bar{v}\eta a} \int_{-1}^{1} dc (1 - c^2) \Gamma \partial_x \phi,$$  \hspace{1cm} (5)

where we have used the relation $\partial_x = a^{-1}\sqrt{1 - c^2}\partial_c$ between the local coordinate $x$ and the cosine of the polar angle $c = \cos \theta$. Sign and magnitude of the velocity are determined by the product of the adsorption factor $\Gamma$ and the derivative of the composition gradient $\partial_c \phi$. A particularly complex behavior occurs for cases as in Fig. 2, where $\Gamma$ takes opposite signs on the two hemispheres and where the integral is dominated by the midplane area.

In Fig. 3 we plot the particle velocity as a function of $\tau = (T_m - T_0)/(T_C - T_0)$, where $T_m$ is the surface temperature at midplane. Critical conditions on the summit of the cap are reached at $\tau_C = 1/\sqrt{2}$, on the particle’s midplane at $\tau_m = 1$, and on the entire surface at $\tau_S = 1 + 1/\sqrt{2}$. The behavior of the velocity is to a large extent determined by the ratio of adsorption parameters $\xi = \Gamma_{\text{unc}}/\Gamma_{\text{cap}}$; that is, by the wetting properties of the two hemispheres. We distinguish three parameter ranges.

(i) For $\tau_C < \tau < 1$, the critical droplet covers only part of the cap, as in the left panel of Fig. 2. Since in this range, $\Gamma$ and $\partial_c \phi$ carry the same sign, the particle moves the cap ahead ($v_p > 0$) for both hydrophobic and hydrophilic coating. The velocity is independent of $\Gamma_{\text{unc}}$.

(ii) In the range $1 < \tau$ and $\xi > 0$, both hemispheres contribute to the integral in \cite{31}. The sudden change of
slope just above $\tau_m$ arises since the maximum derivative $\partial_t \phi$ occurs on the uncapped hemisphere; see the right panel of Fig. 1. The velocity is maximum at $\tau \approx 1.5$, where most of the particle is covered by the critical droplet, then decreases at $\tau_S$, and again increases as $v_p \propto \sqrt{\tau}$ at very strong driving.

(iii) For $1 < \tau$ and $\xi < 0$, the velocity is to a large extent determined by the change of sign of $\phi - \phi_C$ at midplane, where the contributions of the two hemispheres partly cancel in (31). If the adsorption parameter is larger on the uncapped part, $\xi < -1$, it dominates the velocity and finally results in a change of sign; well beyond $\tau_S$ one finds $v_p \propto -\sqrt{\tau}$.

We briefly discuss the above result in view of recent experiments. At small or moderate driving, $\tau \lesssim \frac{3}{2}$, we expect the particles to move the cap ahead. This agrees with observations on carbon-capped silica beads [21], yet contradicts those on gold-capped beads [4] which move the non-coated side ahead. At strong driving, the cap-ahead orientation was found for silica beads with a hydrophobic gold cap, and the opposite behavior for strongly hydrophilic gold caps [19]; these observations are accounted for by the curves of Fig. 3 when assuming large $\tau$ and a strong lutidine affinity for silica [27].

The relation between the laser intensity $I$ and the excess temperature, $T_m - T_0 = I \chi a/2\kappa$, results in [24]

$$v_p \propto \frac{(I - I_C)^2}{\sqrt{a}}, \quad I_C = \frac{\sqrt{2} \kappa}{\chi a} (T_C - T_0)$$

(6)

where $\kappa$ is the heat conductivity and $\chi$ the absorption coefficient per unit area. The power law in intensity is valid in a narrow range only, and thus is not visible in Fig. 3. The cusps at $\tau = \tau_m$ follow the law $(I - I_C)^{1/2}$. The size dependencies of $v_p$ and $I_C$ agree at least qualitatively with experiment [19].

Self-propulsion velocity $v_p$ as a function of $\tau = (T_m - T_0)/(T_C - T_0)$, for different values of absorption parameters. Positive $v_p$ means that the particle moves the cap ahead. We fix the adsorption parameter of the cap and vary the ratio $\xi = \Gamma_{unc}/\Gamma_{cap}$. Self-propulsion sets in at $\tau_C = 1/\sqrt{2}$. If the critical droplet extends to both hemispheres ($\tau > 1$), the velocity strongly depends on $\xi$ and changes sign for $\xi < -1$.

FIG. 3: Self-propulsion velocity $v_p$ as a function of $\tau = (T_m - T_0)/(T_C - T_0)$, for different values of absorption parameters. Positive $v_p$ means that the particle moves the cap ahead. We fix the adsorption parameter of the cap and vary the ratio $\xi = \Gamma_{unc}/\Gamma_{cap}$. Self-propulsion sets in at $\tau_C = 1/\sqrt{2}$. If the critical droplet extends to both hemispheres ($\tau > 1$), the velocity strongly depends on $\xi$ and changes sign for $\xi < -1$.

FIG. 4: Squirmer parameter $\beta$. For $\tau \to \tau_C$, the active area reduces to a small spot, resulting in $\beta = 5$ [24]. The divergence for $\xi = -3$ occurs where the velocity $v_p$ is zero.
Charge effects. We conclude with a discussion of charge effects, which could be at the origin of the backward motion of gold-capped silica beads [4]. When brought in contact with water, many materials acquire a surface charge. Then the mobile counterions and the screened electric field modify the above picture obtained for non-ionic interactions. Charge effects have been shown to be relevant for the reversible aggregation of polystyrene particles in a near-critical water-lutidine mixture [29], and they may even change the sign of the critical Casimir effect [30]. Typical surface charge densities are of the order of $\mu C/cm^2$, that is, one elementary charge per ten square nanometers. This surface charge is screened on the scale of the Debye length $\kappa^{-1}$. In the absence of salt, screening is due to dissociated water, $\kappa^{-1} = 700 \text{ nm}$; added salt or a modified pH reduce this value.

There are two distinct charge effects, the drift of the mobile ions due to the thermodynamic force $-\nabla \mu$, and the non-uniform properties of the electric-double layer [24], similar to those in a temperature gradient [25]. Here we discuss only the ion-drift term. The electrostatic self-energy of a monovalent ion of radius $a_m$ reads

$$\mu = \frac{e^2}{8\pi \varepsilon a_m}. \quad (8)$$

In the non-uniform demixing area, the permittivity $\varepsilon$ varies with the composition $\phi$, as illustrated in Fig. 5. The thermodynamic force density $-\rho \partial_x \mu$, with the ion concentration $\rho$, drags the fluid along the particle surface and thus induces the slip velocity

$$v_s = -\frac{1}{\eta} \int_0^\infty dz z^2 \rho \partial_x \mu. \quad (9)$$

Spelling out the gradient, $\partial_x \mu = -\mu(\partial_x \ln \varepsilon) \partial_x \phi$, assuming that the permittivity of water-lutidine obeys the linear law $\varepsilon = \phi \varepsilon_w + (1-\phi) \varepsilon_l$ [31], and using $\varepsilon_w \gg \varepsilon_l$, one finds $\partial_x \mu \approx -\frac{1}{\mu} \partial_x \phi$. Evaluating the counterion concentration in Debye-Hückel approximation, $\rho = (\varepsilon/\varepsilon_l) \xi (\kappa^{-1})^2$, and interpolating the limits where the screening length $\kappa^{-1}$ is much larger or much smaller than the thickness $\sigma$ of the critical layer, we find for the particle velocity [24]

$$v_p = -\frac{e|\xi|}{8\pi \eta a_m a} \int_{-1}^1 dc \left( \frac{1-c^2}{[1+(\sigma \kappa)^{-1}]^2} \right). \quad (10)$$

In the absence of salt, the ion concentration due to water dissociation ($\sim 3 \times 10^{-6} \text{ nm}^{-3}$) is much smaller than the concentration of counterions released by the charged surface ($\sim 10^{-4} \text{ nm}^{-3}$), and thus has be neglected. Adding salt would result in diffusiophoresis in non-uniform electrolyte [32] [24]. Moreover, we have discarded hydration and dispersion forces, and more generally specific-ion effects [15] [55]. With typical parameters ($\xi \sim -25 \text{ mV}$, $a_m \sim 3 \text{ Å}$) one finds a velocity of the order of microns per second.

According to [10], the particle moves in the direction opposite to the composition gradient, that is, cap-ahead for lutidine-adsorbing coating and cap-behind for water-adsorbing coating. This velocity contribution possibly resolves the above-mentioned discrepancy between [31] and experiments on gold-capped silica particles: Indeed, [10] accounts for both the cap-ahead motion observed for hydrophobic coating and the backward motion for hydrophilic caps [4]. In general, the superposition of [31] and [10] gives rise to an intricate dependence of the motility on charge and wetting properties; a change of a parameter such as salinity or heating power, could switch the sign of the particle’s self-propulsion velocity.

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Here we give the derivation for several results quoted in the main text, in particular the water-lutidine composition \( \hat{\phi} \) in the boundary layer, the corresponding pressure \( P \), and the particle velocity due to non-ionic surface forces and charge effects.

I. STOKES EQUATION IN THE BOUNDARY LAYER

In the vicinity of the critical point \((\phi_C, T_C)\), the water content of the spinodal phases is well approximated by

\[
\phi(r) - \phi_C = \pm \sqrt{\frac{T(r) - T_C}{C}}.
\]

This temperature dependent composition corresponds to a quiescent state of mixture, there is no viscous flow and no diffusion current. The forces exerted by the particle surface on the fluid, however, result in a non-equilibrium state with stationary flows in the boundary layer.

The surface forces are expressed in terms of the interaction of water and lutidine with the solid, resulting in excess energy densities

\[
\hat{u}_i(z) = U_i(z) - U_i(\infty),
\]

where \( U_i(z) \) is the partial energy density of component \( i \), and \( U_i(\infty) \) its bulk value. By definition, \( \hat{u}_w(z) \) and \( \hat{u}_l(z) \) are finite only within a thin layer of thickness \( \lambda \) and vanish at larger distance. For a homogeneous surface the \( \hat{u}_i \) do not depend on the parallel coordinate \( x \), whereas the composition is function of both \( x \) and \( z \).

The following treatment is based on the stationary Stokes equation for the velocity field \( \mathbf{v} \) in the vicinity of the particle,

\[
\eta \nabla^2 \mathbf{v} = \nabla P - \mathbf{f},
\]

with the hydrodynamic pressure \( P \) and the force density exerted by the particle on the fluid,

\[
\mathbf{f} = -\hat{\phi} \nabla \hat{u}_w - (1 - \hat{\phi}) \nabla \hat{u}_l.
\]

II. COMPOSITION

Close to the particle surface, the normal velocity \( v_z \) and its derivatives are negligibly small; thus the normal component of the right-hand side of (13) reduces to \( 0 = \partial_z P - f_z \). Formal integration gives the expression for the pressure,

\[
P(z) = \int_z^\infty dz' \left( \hat{\phi} \partial_z \hat{u}_w + (1 - \hat{\phi}) \partial_z \hat{u}_l \right).
\]

The composition \( \hat{\phi} \) is determined from the excess chemical potential of an ideal binary mixture,

\[
\hat{\mu} = \hat{u}_w - \hat{u}_l + \frac{k_B T}{v_w} \ln \hat{\phi} - \frac{k_B T}{v_l} \ln(1 - \hat{\phi}),
\]

where all quantities depend on position. For the particle surface, the energies vanish \( \hat{u}_i = 0 \), and the composition takes the bulk value \( \phi \).

The composition close to the boundary, \( \hat{\phi} \), is obtained from the condition of constant chemical potential. If the molecular volumes are identical, \( v_w = v_l \), one readily finds

\[
\hat{\phi} = \frac{\phi}{\phi + (1 - \phi) e^{v_w(\hat{u}_w - \hat{u}_l)/k_B T}}.
\]

An approximate form for the general case \( v_w \neq v_l \) is obtained by rewriting the relation \( \partial_z \hat{\mu} = 0 \) in the form

\[
\hat{\phi}(1 - \hat{\phi}) \partial_z (\hat{u}_w - \hat{u}_l) + \left( \frac{\hat{\phi}}{v_l} + \frac{1 - \hat{\phi}}{v_w} \right) k_B T \partial_z \hat{\phi} = 0,
\]

and by replacing the volume factor in the second term on the left-hand side with the constant \( v^{-1} = \phi_C v_l^{-1} + (1 - \phi_C) v_w^{-1} \). The resulting differential equation

\[
\hat{\phi}(1 - \hat{\phi}) \partial_z (\hat{u}_w - \hat{u}_l) + v^{-1} k_B T \partial_z \hat{\phi} = 0
\]

is readily solvable; with the boundary condition \( \hat{\phi}|_{z \rightarrow 0} = \phi \) one finds

\[
\hat{\phi} = \frac{\phi e^{-\hat{u}_w/k_B T}}{\phi e^{-\hat{u}_w/k_B T} + (1 - \phi) e^{-\hat{u}_l/k_B T}},
\]

Inserting this expression in the pressure gradient and integrating, we obtain

\[
P = \frac{k_B T}{v} \ln \left( \phi e^{-\hat{u}_w/k_B T} + (1 - \phi) e^{-\hat{u}_l/k_B T} \right).
\]
Attractive molecular potentials, $\dot{u}_i < 0$, increase the pressure, repulsive forces reduce the pressure. Well beyond the boundary layer, the pressure vanishes, $P = 0$, and the liquid is quiescent.

III. QUASI-SLIP VELOCITY

Within the interaction range, however, the fluid is subject to both to the parallel force component and the pressure gradient, as expressed by the parallel component of Stokes’ equation $\eta \nabla^2 v_x = \partial_x P - f_x$. Since $v_x$ varies much more rapidly in perpendicular direction, the derivatives with respect to $x$ are small, and one has

$$\eta \partial_x^2 v_x = \partial_x P - f_x. \quad (19)$$

Integrating twice gives the effective slip velocity at a distance $\lambda$ from the solid boundary,

$$v_s = \frac{1}{\eta} \int_0^\infty dz \left( f_x - \partial_x P \right). \quad (20)$$

Spelling out the pressure gradient, one finds that the force $f_x$ is cancelled by an opposite term from $\partial_x P$, and that the integrand is proportional to the composition gradient,

$$f_x - \partial_x P = -\frac{k_B T}{\bar{v} \eta} \frac{e^{-\psi_w} - e^{-\psi_i}}{\phi e^{-\psi_w} + (1 - \phi)e^{-\psi_i}} d\phi,$$

where we use the shorthand notation for the effective potential for water and lutidine,

$$\psi_i = \bar{v} \dot{u}_i.$$

Integrating twice and reorganizing the integrals one obtains the slip velocity in the form

$$v_s = -\frac{k_B T}{\bar{v} \eta} \Gamma \frac{d\phi}{dx}, \quad (21)$$

with the adsorption parameter

$$\Gamma = \int_0^\infty dz \frac{e^{-\psi_w} - e^{-\psi_i}}{\phi e^{-\psi_w} + (1 - \phi)e^{-\psi_i}}.$$

For a dilute solution of a single interacting species, the quantity $\Gamma$ is known as the product of the interaction and Gibbs adsorption lengths, $\Gamma = L_{int} L_{ads}$ [2].

It turns out convenient to explicit the adsorption parameter for a square potential of width $\lambda$ and amplitude $\psi_i$,

$$\psi_i = \bar{v} \psi_i \Theta(\lambda - z),$$

where $\Theta(z)$ is the usual step function. Then the adsorption parameter reads

$$\Gamma = \frac{\lambda^2}{2} \frac{e^{-\psi_w} - e^{-\psi_i}}{\phi e^{-\psi_w} + (1 - \phi)e^{-\psi_i}}, \quad (23)$$

$\Gamma$ is positive for $\psi_w < \psi_i$, and negative for $\psi_w > \psi_i$. Estimating the numerical value of $\Gamma$ from measured velocities suggests that the $\psi_i$ are of the order of at most a few percent; then one has to linear order $\Gamma = \frac{1}{2} \lambda^2 (\psi_i - \psi_w)$.

The coordinate $x$ points towards the cap where the temperature is highest. If the particle surface has a strong affinity with water, $\psi_w < \psi_i$, and $\Gamma > 0$. Such a cap is surrounded by a critical droplet which is rich in water, that is, $\phi > \phi_c$. Thus the derivative $\partial_x \phi$ in (21) is positive, and the slip velocity is negative, that is, it points toward the uncapped hemisphere. With the same argument one finds $v_s < 0$ for a hydrophobic surface, where both $\Gamma$ and $\partial_x \phi$ are negative.

We conclude that the slip velocity on the cap is negative, independently of the surface properties. This statement does not necessarily hold true on the uncapped hemisphere: Indeed, if $\Gamma$ takes opposite signs on the two hemispheres, the derivative $\partial_x \phi$ and thus the slip velocity changes sign along the uncapped one; see Fig. 2 of the main text.

IV. SQUIRMER PARAMETER $\beta$

From the multipole expansion of the velocity field, one obtains the first two terms of of the slip velocity [3][4]

$$v_s = -\sin \theta (B_1 + B_2 \cos \theta). \quad (24)$$

The particle velocity is given by the first term, $v_s = \frac{2}{3} B_1$. The interaction of a microswimmer with a wall and collective effects are to a large extent related to the squirmer characteristics

$$\beta = B_2/B_1. \quad (25)$$

A “puller” ($\beta > 0$) is obtained if the slip velocity is dominant on the front hemisphere, and a “pusher” ($\beta < 0$) if the slip velocity is large on the back part.

In order to obtain the squirmer parameter $\beta$ for the particles in a critical mixture, we start from the slip velocity given in the paper,

$$v_s = -\frac{k_B T}{\bar{v} \eta} \frac{d\phi}{dx} = -\sqrt{1 - c^2} \frac{c^2 k_B T}{\bar{v} \eta} \frac{1}{d\phi} \frac{d\phi}{dc}. \quad (26)$$

Using that the adsorption parameter $\Gamma$ takes constant values on the two hemispheres, $\Gamma(c) = \Gamma_{cap} \Theta(c) + \Gamma_{unc} \Theta(-c)$, we find

$$\Gamma \frac{d\phi}{dc} = \frac{d}{dc} (\Gamma \phi - (\Gamma_{cap} - \Gamma_{unc}) \Theta(c)) \equiv \frac{d\Omega}{dc}. \quad (27)$$

Expanding $\Omega$ in Legendre polynomials, $\Omega = \sum_n \Omega_n P_n(c)$, with the coefficients

$$\Omega_n = \frac{2n + 1}{2} \int_{-1}^1 dc \Omega(c) P_n(c),$$

one readily obtains

$$v_s = -\sqrt{1 - c^2} \frac{k_B T}{\bar{v} \eta} (\Omega_1 + 3 \Omega_2 \cos \theta + ...). \quad (28)$$
Thus we have for the squirmer parameter
\[ \beta = 3 \frac{\Omega_2}{\Omega_1}, \] (29)
A particularly simple situation occurs if the active area on the particle is small, such that \( \Omega = \Omega_0(1 - c) \) and \( \Omega_n = \frac{2\Omega_0}{c^2}. \) This case is realized by Janus particles in a near-critical mixture at small driving, resulting in the squirmer parameter
\[ \beta = 5 \quad \text{(weak driving, } q \approx q_C). \] (30)

V. SELF-PROPULSION VELOCITY

A. General

Following the well-known scheme, we calculate the particle velocity by averaging the slip velocity over the particle surface,
\[ v_p = -\langle v_x e_x \rangle = \frac{k_B T}{\bar{v} \eta} \int d\Omega \frac{\Gamma \partial_c \phi}{\sqrt{\Omega}} e_x, \] (31)
with the tangent vector \( e_x. \) The derivative with respect to the local variable \( x \) reads in polar coordinates \( \partial_x = -a^{-1} \partial_\theta, \) which in turn is readily rewritten as
\[ \partial_x = \frac{1}{a} \sqrt{1 - c^2} \partial_c, \]
with the cosine of the polar angle \( c = \cos \theta. \) Projecting the tangent vector \( e_x \) on the particle axis gives \( e_x \cdot e_p = \sin \theta = \sqrt{1 - c^2}, \) and we find
\[ v_p = e_p \frac{k_B T}{2 \bar{v} \eta a} \int_{-1}^1 dc (1 - c^2) \Gamma \partial_c \phi, \] (32)
where \( e_p \) points toward the cap. If \( \Gamma \partial_c \phi > 0, \) the particle moves the cap ahead.

The integrand in \( (32) \) may take different magnitudes and even opposite signs on the bare and capped parts of the particle surface. We further simplify by taking \( \Gamma \) as a constant on each hemisphere. Noting \( \Gamma_{\text{cap}} \) for the metal capped half and \( \Gamma_{\text{unc}} \) for the remaining one, we find the self-propulsion velocity
\[ v_p = \frac{k_B T}{2 \bar{v} \eta a} \left( \Gamma_{\text{cap}} \int_{-1}^1 dc (1 - c^2) \partial_c \phi + \Gamma_{\text{unc}} \int_{-1}^1 dc (1 - c^2) \partial_c \phi \right). \] (33)

The cap contribution is always positive. A negative velocity may result, if \( \Gamma_{\text{cap}} \) and \( \Gamma_{\text{unc}} \) carry opposite signs and if \( \Gamma_{\text{sum}}/\Gamma_{\text{cap}} > -1. \)

From \( (31) \) one obtains \( \partial_c \phi \) in terms of the temperature derivative
\[ \partial_c \phi = \pm \frac{\partial_c T}{2 \sqrt{C(T - T_C)}}, \] (34)

B. Weak-driving behavior

We evaluate \( (33) \) for the case of weak driving, where the heating power \( I \) hardly exceeds the critical value \( I_C. \) Then the critical conditions are satisfied only on a small area close to the summit of the cap. Linearizing the surface excess temperature about its value at \( c = 1, \)
\[ T(c) - T_0 = (T_{\text{sum}} - T_0)(1 - \beta + \beta c), \] (35)
defining the relative excess temperature with respect to \( T_C, \)
\[ \frac{T_{\text{sum}} - T_0}{T_C - T_0} = 1 + \delta, \] (36)
and inserting \( (31), \) we find for the particle velocity
\[ v_p = \frac{k_B T \Gamma_{\text{cap}}}{4 \bar{v} \eta a} \sqrt{\frac{T_C}{T}} F(\beta, \delta), \]
with
\[ F(\beta, \delta) = \int_{c_0}^1 dc \frac{(1 - c^2) \beta(1 + \delta)}{\sqrt{(1 - \beta(1 - c)(1 + \delta)) - 1}}. \] (37)
The critical conditions are satisfied on the patch defined by \( c > c_0, \) with
\[ c_0 = \frac{1 - (1 - \beta)(1 + \delta)}{\beta(1 + \delta)}. \]
The integral results in
\[ F(\beta, \delta) = \frac{8 \beta(1 + \delta) - \frac{2}{3} \delta}{\beta^2 (1 + \delta)^2} \delta^{\frac{2}{3}}, \] (38)

The above approximation is valid for small excess temperature, \( \delta \ll 1. \) Evaluate the integral to lowest order \( \delta \) and putting \( \beta = \frac{1}{8}, \) we obtain
\[ v_p = \frac{k_B T \Gamma_{\text{cap}}}{8 \bar{v} \eta a} \sqrt{\frac{T_C}{C}} \frac{64}{3} \delta^{\frac{2}{3}} (1 + O(\delta)). \] (39)

With temperature field of the thin-cap limit ?? we have \( T_{\text{sum}} - T_0 = \sqrt{2}(T_m - T_0), \) and thus
\[ \delta = \sqrt{2} \frac{T_m - T_0}{T_C - T_0} - 1. \]

Expressing the excess temperature in terms of the heating power, \( \sqrt{2}(T_m - T_0) = I_N \sqrt{\alpha/2 \kappa}, \) with the heat conductivity \( \kappa \) and the absorption coefficient \( \chi, \) we find
\[ \delta = \frac{\chi a}{\sqrt{2 \kappa} T C} (I - I_C). \]

Thus we obtain the behavior of the particle velocity at the onset of self-propulsion,
\[ v_p = \frac{k_B T \Gamma_{\text{cap}}}{8 \bar{v} \eta a} \sqrt{\frac{\chi a}{2 C T C \kappa^3}} \frac{(I - I_C)^{\frac{1}{2}}}{\sqrt{\alpha}}. \] (40)

Note that \( v_p \) increases with the excess power as \( (I - I_C)^{\frac{1}{2}} \) and is inversely proportional to the square root of the particle radius. From \( (38) \) it is clear, however, that this power law is valid in a very narrow range only.
VI. CHARGE EFFECTS

When brought in contact with water, most materials acquire a surface charge and release counterions or protons. Here we show how the resulting electrostatic effects modify the picture obtained from non-ionic surface forces. Typical surface charge densities are of the order of $\mu C/cm^2$, which corresponds to one elementary charge on several square nanometers. This surface charge is screened on the scale of the Debye length $\kappa^{-1} = \sqrt{\varepsilon T/2n_0 e^2}$ where $\varepsilon$ is the solvent permittivity and $n_0$ the electrolyte strength. For pure water at pH 7 one has $\kappa^{-1} = 700$ nm, added salt or a modified pH significantly reduce this value.

In the non-uniform demixing area, the electric properties in the double-layer vary with the composition $\phi$. There are two contributions to the slip velocity, the first of which arises from the non-uniform permittivity and salinity, and the second one from the solvation energy of the mobile ions. The discussion of these terms closely follows the treatment of the electric-double layer in a temperature gradient [3].

A. Electric double layer

We start from the stationary Stokes equation

$$\eta \nabla^2 \mathbf{v} = \nabla P - \nabla \cdot \mathbf{T},$$

where the source term is given by the osmotic pressure of the mobile ions, $P$, and the electrostatic stress tensor $\mathbf{T}$. Accounting for non-uniform permittivity $\varepsilon$ and salinity $n_0$, yet discarding the (weak) temperature gradient, one has

$$\nabla P - \nabla \cdot \mathbf{T} = \frac{1}{2} E^2 \nabla \varepsilon + \frac{n}{n_0} k_B T \nabla n_0,$$

where $n$ is the electrolyte strength within the double layer, and $E = -\partial_x V$ the perpendicular electric field.

In Poisson-Boltzmann mean-field theory the electrostatic surface potential reads as

$$V = (4k_B T/e) \ln \tanh(\nu e^{-\kappa z}),$$

with the dimensionless parameter

$$\nu = \tanh \frac{e \zeta}{4k_B T},$$

and the zeta-potential $\zeta$. The salinity factor reads $n/n_0 = \cosh(\nu V/k_B T)$. Integrating Stokes’ equation with the appropriate boundary equations, one finds the slip velocity

$$v_s = -\frac{1}{\eta} \int_0^\infty dz z \left( \frac{1}{2} E^2 \partial_x \varepsilon + 2 \left( \frac{n}{n_0} - 1 \right) k_B T \partial_x n_0 \right).$$

In the following we resort to the Debye-Hückel approximation,

$$V = (4k_B T/e) \nu e^{-\kappa z},$$

where we keep the parameter $\nu$ for notational convenience. Thus we find

$$v_s = -\nu^2 \frac{2k_B T \kappa^2}{\pi \eta \ell_B} \partial_x \ln(\varepsilon n_0) \int_0^\infty dz z^2 e^{-2\kappa z} \partial_x \phi(z).$$

In the second equation we have used the definition of the screening length $\kappa^{-1}$ and the Bjerrum length $\ell_B = e^2/4\pi\varepsilon k_B T$, and we have assumed that the spatial variation of $\varepsilon$ and $n_0$ is due to their composition dependence.

The value of the integral in (47) depends on the ratio of the screening length $\kappa^{-1}$ and of the thickness of the critical layer, $\sigma$. For the sake of simplicity, we approximate the variation of the gradient with the distance from the particle surface as $\partial_x \phi(z) = \partial_x \phi(0) e^{-z/\sigma}$, and thus find

$$v_s = -\nu^2 \frac{k_B T}{2\pi \eta \ell_B} \partial_x \ln(\varepsilon n_0) \frac{(2\kappa \sigma)^2}{(1 + 2\kappa \sigma)^2} \partial_x \phi.$$

B. Ion solvation energy

The second mechanism is related to the ion solvation energy; the electrostatic self-energy of a monovalent molecular ion of radius $a_m$ contributes to its chemical potential the term

$$\mu = \frac{e^2}{8\pi \varepsilon a_m}.$$  

The thermodynamic force on each ion, $-\nabla \mu$, results in a diffusion current which in turn drags the liquid with the slip velocity

$$v_s = \frac{1}{\eta} \int_0^\infty dz z \rho(z) \partial_x \mu.$$

Retaining the composition dependence of the permittivity, we have $-\nabla \mu = \mu(d \ln \varepsilon / d \phi) \nabla \phi$. In Debye-Hückel approximation, the ion concentration reads $\rho(z) = \kappa^2 |\nu|(4k_B T/e) e^{-\kappa z}$. We thus have

$$v_s = \frac{\kappa^2 |\nu| k_B T}{2\pi \eta a_m} \partial_x \ln \varepsilon \int_0^\infty dz z e^{-\kappa z} \partial_x \phi.$$

Approximating the composition gradient as $\partial_x \phi(z) = \partial_x \phi(0) e^{-z/\sigma}$, we find

$$v_s = \frac{|\nu| k_B T}{2\pi \eta a_m} \partial_x \ln \varepsilon \frac{(\kappa \sigma)^2}{(1 + \kappa \sigma)^2} \partial_x \phi.$$
C. Composition dependence

The above slip velocities arise from the fact that permittivity and salinity vary due to the non-uniform composition of the solvent. As the simplest model we assume an ideal-mixture behavior, e.g., \( \varepsilon = \phi \varepsilon_w + (1 - \phi) \varepsilon_l \). Noting that the permittivity is much larger in water than in lutidine, \( \varepsilon_w / \varepsilon_l \approx 13 \), one finds for the derivative

\[
\partial_\phi \ln \varepsilon \approx 1. \tag{53}
\]

Such a linear law has been observed for water-alcohol mixtures \(^5\), and a similar relation may be assumed for the salinity.

In addition to the permittivity variation, the ions are subject to hydration and dispersion forces which are not necessarily smaller than the electrostatic effect. It turns instructive to compare with thermal diffusion of molecular ions in a temperature gradient. Then the electrostatic self-energy changes due to the permittivity \( \varepsilon(T) \), resulting in the thermodynamic force

\[
-\nabla \mu = \mu d \ln \varepsilon \nabla T / d \ln T. \tag{54}
\]

Since the logarithmic derivative is negative, \( d \ln \varepsilon / d \ln T \approx -1.4 \) at room temperature, one expects the ions to migrate opposite to the thermal gradient, that is, toward colder regions of the sample. This is indeed observed for almost all ions, yet with prefactors that may differ by one order of magnitude. Quite generally, a much stronger effect is observed for ions containing protons, such as \( \text{H}_3\text{O}^+ \), \( \text{OH}^- \), and quaternary ammonium cations such as TEA \(^9\).

D. Sign of the particle velocity

Comparing the two contributions to the slip velocity \(^47\) and \(^51\), one finds that the electric-double layer and solvation energy contributions have similar factors but carry opposite signs. The particle velocity is given by the surface average \( v_p = -\langle \mathbf{v}_s \rangle \).

\[
v_p = -\frac{k_B T}{2\pi \eta a} \left( \frac{|\nu|}{a_m} f_1 - \frac{\nu^2}{\ell_B^2} f_2 \right), \tag{55}
\]

where the dependence on the screening length and the thickness of the critical layer is accounted for by the factors

\[
f_n = \frac{\kappa^2}{2} \int_{-1}^{1} dc (1 - c^2) \int_0^{\infty} dz z e^{-\kappa \sigma z} \partial_\sigma \phi(z), \tag{56}
\]

with \( n = 1, 2 \).

Simplifying the variation of \( \partial_\sigma \phi(z) \) with \( z \) and proceeding as in \(^{31}\), we find

\[
f_n = \frac{1}{2} \int_{-1}^{1} dc (1 - c^2) \frac{(\mu f_1)}{(1 + \mu f_2)^2} \partial_\sigma \phi. \tag{57}
\]

As the most important difference, the double-layer term is quadratic in \( \nu \), whereas the solvation energy contribution is linear. Since the coupling parameter is smaller than unity, one has \( \nu^2 < |\nu| \). Moreover, the ion radius is in general smaller than the Bjerrum length, that is, \( 1 / \ell_B < 1 / a_m \). The factors \( f_n \) involving \( \kappa \sigma \) provide an opposite effect, for \( \kappa \sigma \ll 1 \) one has \( f_1 / f_2 = \frac{1}{4} \) and \( f_1 / f_2 = 1 \) for \( \kappa \sigma \rightarrow 1 \).

A surface potential of \( 27 \) mV corresponds to the thermal energy, \( \varepsilon \zeta = k_B T \), and results in \( \nu = \frac{1}{4} \). Thus for weakly charged surfaces, the second term in \(^{55}\) is small, and the particle velocity takes the opposite sign of the derivative of the order parameter, \( \partial_\sigma \phi \).

VII. MISCELLANEOUS REMARKS

A. Temperature profile

We have assumed that the thermal conductivity is roughly constant, which is well justified for thin caps. A sufficiently thick gold cap, however, is almost an isotherm \(^4\), thus strongly reducing the weight of the active hemisphere \( \langle c \rangle \geq 0 \) in \(^{51}\). Then the behavior of \( v_p \) is well described by the curves with large \( |\xi| \), and the particles are mostly pushers \( (\beta < 0) \).

B. Thickness of liquid phase boundary

For Janus particles with opposite affinities on the two hemispheres, the critical droplet separates in water-rich and lutidine-rich compartments. The composition through the phase boundary has been modelled by the simple form \( \phi \tanh(\xi/c_0) \), with the cosine of the polar angle \( c = \cos \theta \) and the parameter \( c_0 = 0.1 \). The relatively large value for \( c_0 \) has been chosen in order to visualize the phase boundary in the plots of Fig. 2. Taking \( c_0 = 10^{-2} \) or \( c_0 = 10^{-3} \) does not modify the particle motility, and in particular leaves the velocity and the squirmer parameter unchanged.

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