A lattice Boltzmann model for self-diffusiophoretic particles near and at liquid-liquid interfaces

Lucas S. Palacios, Andrea Scaglioni, Ignacio Pagonabarraga

Institute for Bioengineering of Catalonia (IBEC), The Barcelona Institute of Science and Technology (BIST), Baldari i Reixac 10-12, 08028 Barcelona, Spain.

Istituto per le Applicazioni del Calcolo, CNR - Via dei Taurini 19, 00185 Rome, Italy

INFN, Sezione di Roma “Tor Vergata”, Via della Ricerca Scientifica 1, 00133 Rome, Italy

Departament de Física de la Materia Condensada, Universitat de Barcelona, Carrer Martí i Franquès 1, 08028 Barcelona, Spain

Universitat de Barcelona Institute of Complex Systems (UBICS), Universitat de Barcelona, 08028 Barcelona, Spain

CECAM, Centre Européen de Calcul Atomique et Moléculaire, Ecole Polytechnique Fédérale de Lausanne (EPFL), Avenue Forel 2, 1015 Lausanne, Switzerland

We introduce a novel mesoscopic computational model based on a multiphase-multicomponent lattice Boltzmann method for the simulation of self-phoretic particles in the presence of liquid-liquid interfaces. Our model features fully resolved solvent hydrodynamics and, thanks to its versatility, it can handle important aspects of the multiphysics of the problem, including particle wettability and differential solubility of the product in the two liquid phases. The method is extensively validated in simple numerical experiments, whose outcome is theoretically predictable, and then applied to the study of the behaviour of active particles next to and trapped at interfaces. We show that their motion can be variously steered by tuning relevant control parameters, such as the phoretic mobilities, the contact angle and the product solubility.

I. INTRODUCTION

Artificial micromotors have gained an ever-growing interest, in recent years, as biomimetic devices and for their manifold microfluidic applications [1]. Being able to convert ambient energy into autonomous motion, they fall in the realm of active matter [2]. A paradigmatic example of model micromotors is provided by self-phoretic particles (SPPs), which self-propel exploiting the phenomenon of colloidal phoresis [3] in the inhomogeneous solute distribution generated by a chemical reaction or a phase transition locally occurring at their surfaces. SPPs include Janus metallic rods [4], catalytic [1, 5, 6] and light-activated Janus colloids [7, 8], among others (see also [9–11] and references therein for reviews). Extensively studied are suspensions of platinum coated, micron-sized polymeric spheres in an aqueous solution of hydrogen peroxide, the latter undergoing a decomposition reaction catalyzed by the platinum into water and oxygen. For this reason, in what follows we will often refer to the solute as oxygen; however, as it will be made clear, the model simply requires the generation and diffusion of a scalar field. The approach is, therefore, more general and can simulate SPPs based on different mechanisms, like the critical water-lutidine demixing [12], or even self-thermophoretic colloids [13, 14]. Despite the consistent body of theoretical, computational and experimental works witnessed, many questions remain still unanswered in the physics of SPPs, especially when it comes to more complex environments than the bulk of a fluid, as, e.g., in the presence of interfaces [11]. As a matter of fact, how the motion of these active particles could be modified or steered by the presence of an interface is not yet totally understood. Recent studies have focused on solid-liquid interfaces [15–17], liquid-liquid interfaces [18–21] or even on a combination of both [22], but a theoretical/computational approach taking into account hydrodynamics and a thermodynamically consistent modelling of the multiphase solute-solvent-particle system is so far missing. Indeed, liquid-liquid interfaces add extra degrees of freedom to the system, owing to their deformability and to the solid phase wetting properties, thus significantly enriching the particle dynamics. Given also the intrinsic out-of-equilibrium physics of active particles, it appears clear how modelling may represent a challenging task.

In this paper, we propose a mesoscopic numerical model, based on a multiphase lattice Boltzmann method, featuring a free energy functional depending on two phase fields that describe the two immiscible component mixture (e.g., oil and water) and the product (oxygen), respectively. The suspended solid particles are endowed with the capability of performing diffusiophoretic motion and of generating a solute field, which stems from the activity of the catalytic site. The method proves, then, able to handle at the same time solvent hydrodynamics, particle-solute interactions, giving rise to the self-propulsion, wettability and preferential solubility of oxygen, that can, in general, accumulate more in one of the two liquid phases, thus allowing to simulate different combination of immiscible fluids.

The paper is organized as follows. In Sec. I1 the thermodynamic model is introduced and tested together with the description of the fluid-solid coupling and of the
implementation of the self-diffusiophoresis. In Sec. III we present the model validation against controlled setups, starting with that of an isolated SPP in a single phase fluid and then moving to the case of mixtures, distinguishing between active and inactive particles, in order to disentangle the effects of capillary and phoretic forces. We report results showing that the relative position and orientation of a self-phoretic Janus particle and an interface depend, in a non-trivial way, on wettability, phoretic mobilities and oxygen solubility. Our findings suggest, then, that a proper tuning of such parameters may enable the guidance of active particles in non-homogeneous fluid media. Conclusions and perspectives are drawn in the final Sec. IV.

II. COMPUTATIONAL MODEL

A suspension of active particles in presence of liquid-liquid interfaces consists of a fluid phase (solvents + solute) and a solid phase (the active particles). To model such a multiphase (and multicomponent) system we resort to a mesoscopic approach, based on the lattice Boltzmann (LB) method [23–25] in the phase field formulation [20, 28].

A. Phase field model: the free energy functional

The fluid phase is a ternary mixture made of two immiscible liquids (say, water and oil) and a solute, which is the product of the reaction occurring at the catalytic site on the particle surface (the oxygen). We associate to the water-oil system a scalar field $\psi(r,t)$ standing for the local composition, that is $\psi = \frac{\rho_W - \rho_O}{\rho_W + \rho_O}$, where $\rho_W$ and $\rho_O$ are the density fields of water and oil, respectively. As in the standard Cahn-Hilliard theory, the thermodynamics of the oil-water mixture is controlled by a quartic in $\psi$ double-well free energy density of Landau type, $f_{ow}[\psi] = A \psi^4 + B \psi^2$ (with $A > 0$ and $B < 0$). This free energy has to be extended to embrace the dynamics of the oxygen, that is, in principle, miscible with each of the two other components; therefore we need to add a term characterized by a single minimum that disregards the energetic cost associated to the concentration gradients [29], such that, in the case of a single component solvent ($f_{ow} = 0$ identically), a diffusive equation for the solute is recovered. A simple parabolic potential is appropriate to this aim (as we will show shortly), namely $f_{ow}(\phi) = \frac{C}{2} \phi^2$ ($C > 0$), having introduced the field $\phi(r,t)$. In actual systems, though, the oxygen may display, in general, a greater affinity for one of the two liquids (it can be more soluble in water than in oil, or vice versa). To account for this preferential concentration an "interaction" term, coupling $\phi$ and $\psi$, has to be included. We propose to do so by simply shifting the global minimum of $f_{ow}(\phi) = 0$ to a $\psi$-dependent minimum, i.e. $f_{ow}(\phi) = \frac{C}{2} \phi^2 \rightarrow f_{ow}(\phi,\psi) = \frac{C}{2} (\phi - \phi_0(\psi))^2$. For $\phi_0(\psi)$ we choose the form $\phi_0(\psi) = \phi_0 + E \tanh(\psi)$, where the parameter $E$ tunes the oxygen solubility and $\phi_0$ sets the average oxygen concentration. The full free energy functional then reads:

$$F[\psi, \phi] = \int d\mathbf{r} \left[ \frac{A}{4} \psi^4 + \frac{B}{2} \psi^2 + \frac{\kappa}{2} |\nabla \psi|^2 + \frac{C}{2} (\phi - E \tanh(\psi) - \phi_0)^2 \right].$$ (1)

Hereafter we set $B = -A$, such that the $\psi$ minima, corresponding to the bulk water and oil phases, are located in $\psi = \pm 1$. The minimization of the functional (1) yields the chemical potentials $\mu_\phi = \frac{\partial F}{\partial \phi}$ and $\mu_\psi = \frac{\partial F}{\partial \psi}$:

$$\mu_\phi = C(\phi - E \tanh(\psi) - \phi_0)$$
$$\mu_\psi = A(\psi^3 - \psi) - \kappa |\nabla \psi|^2 - C E \frac{(\phi - E \tanh(\psi) - \phi_0)}{\cosh^2(\psi)} \right].$$ (2)

The dynamics of the ternary mixture system is, then, described by the following equations:

$$\partial_t \phi + \nabla \cdot (\mathbf{u} \phi) = D_\phi \nabla^2 (\phi - \phi_0(\psi)) + D_\phi - k_d(\phi - \phi_0(\psi))$$
$$\partial_t \psi + \nabla \cdot (\mathbf{u} \psi) = D_\psi \nabla^2 \left( \psi^3 - \psi - \frac{\kappa}{A} |\nabla \psi|^2 - E \frac{\phi - \phi_0(\psi)}{\cosh^2(\psi)} \right).$$ (3)
where \( D_\phi = C M_\phi \) and \( D_\psi = A M_\psi \) are the diffusivities for the oxygen and the water-oil mixture, respectively, and \( M_\phi \) and \( M_\psi \) are the mobility constants for \( \phi \) and \( \psi \). The equation for \( \phi \) has been equipped with a source term, \( D_\phi \), that accounts for the generation of oxygen in a reaction catalyzed by the particles (see next section for further details). This production needs to be balanced by a sink term, \( k_d(\phi - \phi_0(\psi)) \), in order to allow the attainment of a steady state. Physically, the sink mimics the degradation of the production or its loss in the environment. Fig. 1 displays the effect of changing the solubility parameter from negative to positive values, by plotting the average oxygen concentration, \( \langle \phi \rangle_{O,W} \) in oil or water as a function of \( E \), at equilibrium and in the absence of particles (hence of oxygen production). Since, by virtue of Eq. (2), the equilibrium profile of \( \phi \) is \( \phi = E \tanh(\psi) \) (the background value having been set to zero here, \( \phi_0 = 0 \)), the average, up to terms of infinitesimal order in \( \xi/L \) (\( \xi \) being the interface width and \( L \) the system size), is \( \langle \phi \rangle_{O,W} \approx \pm E \tanh(1) \), where the positive/negative corresponds to the average being taken over the oil or water phase, respectively; this prediction is reported in Fig. 1 with solid lines and agrees well with the numerical data.

\[
\langle \phi \rangle_{O,W} = \pm E \tanh(1)
\]

![Equilibrium oxygen concentration](image)

**FIG. 1.** Equilibrium oxygen concentration, averaged respectively over the water (blue crosses) and oil (orange squares) phases, as a function of the \( E \) parameter. The solid lines represent the expectations from the thermodynamic model, \( \langle \phi \rangle_{O,W} \approx \pm E \tanh(1) \), where the positive/negative sign corresponds to oil/water and is depicted in violet/yellow. The simulation were run with \( \phi_{\text{bio}} = 0 \).

### B. Particles

Particles are modelled as solid spheres defined by a set of boundary “links” between inner and outer nodes. The fluid-solid coupling is realized by means of the so-called “bounce-back-on-links” algorithm that guarantees the proper momentum-torque exchange between particles and solvent. The colloidal phoresis is introduced by imposing at the particle surface an effective slip velocity profile which depends on the local solute concentration as:

\[
v_s = \mu(r_s)(1 - \hat{n} \times \hat{m}) \cdot \nabla \phi \tag{4}
\]

where \( r_s \) is a point on the surface of the particle, \( \hat{m}(r_s) \) is the normal to the surface in \( r_s \) and \( \mu(r_s) \) is the phoretic mobility at \( r_s \), which carries the molecular details of the solute-colloid interaction. As a consequence, in the presence of concentration gradients, particles gain a net propulsion velocity \( V_p \approx -\mu \nabla \phi \) (for uniform phoretic mobility \( \mu(r_s) \equiv \mu \)), hence if \( \mu < 0 \) they are attracted by the solute, else if \( \mu > 0 \) they are repelled. To achieve self-propulsion, particles are, then, endowed with the property of generating solute: this is done by simply adding a production term that injects \( \phi \) with a given rate at nodes neighbouring the particle surfaces, thus modelling the catalytic activity of Pt-coated colloids. In particular, a Janus activity profile is chosen:

\[
\Pi(r_s) = \begin{cases} 
\alpha & \text{if } \hat{m} \cdot \hat{n}(r_s) \leq 0 \\
0 & \text{if } \hat{m} \cdot \hat{n}(r_s) > 0 
\end{cases} 
\tag{5}
\]

where \( \alpha \) is the constant production rate and \( \hat{m} \) is the particle characteristic unit vector (see the sketch in Fig. 2A)). Notice that the superposition of such activities associated to the various particles is precisely what gives rise to the production term \( D_\phi \) appearing in Eq. (3).

Analogously, for the phoretic mobility \( \mu(r_s) \) we set:

\[
\mu(r_s) = \begin{cases} 
\mu_- & \text{if } \hat{m} \cdot \hat{n}(r_s) \leq 0 \\
\mu_+ & \text{if } \hat{m} \cdot \hat{n}(r_s) > 0 
\end{cases} 
\tag{6}
\]

For an isolated Janus particle with the above activity and mobility profiles we expect a motion with constant velocity of magnitude:

\[
v_p = \frac{|(\mu_+ + \mu_-)\alpha|}{8D} \tag{7}
\]

In the presence of interfaces a specific treatment of the interaction of the two liquids with solid boundaries, which determines the particles wetting properties, needs to be included. To this aim, an extra boundary term is added to the free energy functional, such that:

\[
F_{\text{int}}[\phi, \psi] = F[\phi, \psi] + \int_S H \psi(r_s) dr_s \tag{8}
\]

where the integral is over the solid surface. The parameter \( H \) controls the wetting through the following boundary condition, that can be derived by minimization of the
surface term in $\psi$, 

$$H = \kappa |\nabla \psi \cdot \hat{n}|$$  \hspace{1cm} (9)

and, therefore, it sets the particle contact angle $\theta_c$, to which it is related by 37

$$\cos(\theta_c) = \frac{1}{2} \left[ -(1 - h)^{3/2} + (1 + h)^{3/2} \right]$$  \hspace{1cm} (10)

where $h = H \sqrt{1/(\kappa A)}$.

C. Numerical details

We simulate numerically the model just introduced on three-dimensional periodic lattices of sizes ranging between $32^3$ to $64 \times 96 \times 96$ (with unit spacing, $\Delta x = 1$). The two liquids have the same kinematic viscosity, equal to $\nu = 1/6$, and same density $\rho = 1$, in lattice Boltzmann units (lbu). The free energy parameters are set to $A = C = 0.0625$, $\kappa = 0.04$, such that the surface tension is $\sigma = (2/3)\sqrt{2\kappa A} \approx 0.047$, and the mobilities are $M_\psi = 0.4$ and $M_\phi = 0.8$, giving the diffusion coefficients $D_\psi = 0.025$ and $D_\phi = 0.05$. The particle radius is fixed to $R = 4.5$. The activity is varied in the range $\alpha \in [0, 10^{-2}]$ and the phoretic mobilities in $\mu_{\pm} \in [0, 0.6]$ (we consider only oxyrepulsive particles). Correspondingly, the largest Reynolds, Mach and Péclet numbers are of the order $Re \approx 0.1$, $Ma \approx 0.03$ and $Pe \approx 3$ (although in most of the simulations we have $Pe \approx 0.1$), thus we are legitimately in an incompressible creeping flow regime.

Unless otherwise specified, the system is initialized with two slabs of oil and water separated by a flat interface (actually two, due to the periodic boundary conditions), corresponding to the equilibrium hyperbolic tangent profile $\psi(r, 0) = \tanh(x/\xi)$. The oxygen field is initially set to $\phi(r, 0) = 0$, everywhere, and then let equilibrate.

III. RESULTS AND DISCUSSION

A. Motion of a Janus particle in a single phase fluid

As a validation of the model, we first consider the motion of an isolated active particle in the bulk of a single phase fluid ($A = E = \kappa = 0$ and $\psi = 0$, identically). Fig. 3A reports the results of a set of simulations aimed at tuning the degradation rate $k_d$. We notice, first of all, from the plot of the space-averaged oxygen concentration, $\langle \phi \rangle(t)$, vs time (in the inset), that the introduction of the sink term works as expected and a steady state is reached. The stationary value, $\langle \phi \rangle_{\infty}$, will depend, of course, on both the particle activity and the degradation rate, as shown in the main panel of the same figure. In particular, it grows with $\alpha$ and decreases with $k_d$. The presence of a linear degradation term implies that the concentration field does not decay purely algebraically with the distance from the source (the particle surface) but it is modulated by an exponential factor, $\phi(r) \sim e^{-r/\ell}/r$, with screening length $\ell = \sqrt{D/k_d}$. In the remainder of the paper the value of the degradation rate is kept fixed to $k_d = 10^{-3}$, which gives a screening length of approximately one particle diameter, $\ell \approx 2R$.

In Fig. 3B we check the dependence of the particle speed on the phoretic mobilities, at fixed activity $\alpha = 10^{-3}$, plotting $v_p$ vs $\mu_-$ (the mobility value on the active side) for various values of the mobility on the opposite cap, $\mu_+$. As expected from the theoretical prediction, Eq. (17), the speed grows linearly with $\mu_-$ (and $\mu_+$). The linearity de-
teriorates a bit as $\mu_+$ increase, probably due to the fact that the Péclet number is also increasing and tends to approach unity (we recall that the result \( \frac{\mu}{\mu_E} \equiv 1 \) is derived under the assumption of vanishing $Pe$ \[ Eq. \[ 33 \] ).

B. Inactive Janus particles at liquid-liquid interfaces

Before facing the problem of active particle motion, a needed preliminary step is to investigate the interaction of an inactive diffusiophoretic particle with the interface, in order to analyze the competing effect of capillary and phoretic forces. To this aim, first we focus on a particle with $\alpha = 0$ and uniform phoretic mobility, $\mu_+ = \mu_\pm = \mu$, initially placed either in oil, water or at the interface, depending on whether it is hydrophobic ($\theta_c = 0^\circ$), neutral ($\theta_c = 90^\circ$) and hydrophilic ($\theta_c = 180^\circ$). Because of the imbalance of capillary and phoretic forces, the particle will relax from its initial position towards or away from the interface. We then monitor its equilibrium position relative to the interface, \( \Delta X = X_{CM} - X_{int} \), as a function of $\mu$ and the oxygen solubility parameter $E$. The results are shown in Fig. 4. When particles are placed in the bulk of the oil or water phases, being the surrounding solute homogeneous, diffusiophoretic forces vanish and $\mu$ and $E$ do not affect the particle motion. Conversely, particles initially trapped at the interface are surrounded by an inhomogeneous solute field, and diffusiophoretic forces become relevant. In particular, the larger is the difference of solute concentration in the two phases (i.e., for growing $|E|$), the stronger are these forces and the further they push the particle away from the interface. At the same time, phoretic forces depend on the strength of the particle-solute interaction, therefore increasing $|\mu|$ has the same effect as increasing $|E|$. More formally, at mechanical equilibrium difference of capillary and phoretic forces balance each other along the normal to the interface, that is $F_{\text{cap}} = F_{\text{ph}}$. The phoretic force is proportional to the concentration gradient, $F_{\text{ph}} \sim - \mu \nabla \phi$; next to the interface, we can approximate $\phi$ with a linear profile, by virtue of $\phi = E \tanh(\psi) = E \tanh(-\tanh(x/\xi)) \approx -2Ex/\xi$, such that the force reads, $F_{\text{ph}} \approx 2\mu E/\xi \propto \mu E$. For small interface deformations, capillarity acts as a Hookean restoring force, with an effective elastic constant proportional to the surface tension \[ Eq. \[ 33 \] , i.e. $F_{\text{cap}} \propto \sigma \Delta X$, whence

$$\Delta X \equiv X_{CM} - X_{int} \propto \mu E, \quad (11)$$

which explains the behaviour emerging from Fig. 4.

We next consider the case of inhomogeneous phoretic mobilities, $\mu_\pm \neq \mu_+ \pm \mu_\pm$, when an oxygen concentration gradient is present at the interface, $E \neq 0$. We set $E = -0.5$, that leads to a larger oxygen concentration in the oil phase, and impose neutral wetting ($\theta_c = 90^\circ$). The particle is initially placed at the interface and aligned with it, i.e. its characteristic vector $\hat{m}$ lies in the interface plane and it is, then, orthogonal to the concentration gradient, $\hat{m} \perp \nabla \phi$. Consequently, due to the phoretic mobility mismatch, the particle is subject to a torque. We will consider here, therefore, both the equilibrium displacement and the equilibrium orientation angle, $\theta$, with respect to the interface, as functions of $\mu_-$ for different $\mu_+$ values.

As expected, Fig. 5A shows that the particle relaxes to a position progressively further from the interface as the phoretic mobilities are increased. Interestingly, though, the equilibrium position saturates at a finite distance from the interface when $\mu_- > \mu_+ > 0$. These observations are better understood looking at Fig. 5B, where the equilibrium orientation angle $\theta$ is plotted. The phoretic torque induced rotation undergone by the particle is faster if the difference between both mobilities is larger, as expected (see inset of Fig. 5B). Because particles re-orient fast with the stronger phoretic mobility facing the water region, the side facing the oil is the more important input to displace the particle from the interface. Hence, this explains why in Fig. 5A we reach a saturation when $\mu_- > \mu_+$.

C. Active Janus particles and liquid-liquid interfaces

Once the inherent behaviour of capillarity and wetting properties on passive Janus colloids has been established, we focus on the behavior of active Janus colloids, $\alpha \neq 0$, with a uniform phoretic mobility profile ($\mu_\pm = \mu_\pm = \mu$). Initially, we consider neutrally-wetting particles trapped at the interface, and analyze their motion at varying $\mu$ and the oxygen solubility parameter $E$, quantifying the product concentration ratio at the two sides of the interface. The values $\mu = 0.3$ and $\mu = 0.5$, and $E = -0.5, E = -0.25, E = 0$ (corresponding to no concentration mismatch) are used. We run simulations starting with different particle orientations defined by $\theta_p$, which is the angle between the particle characteristic vector and the interface (See Fig. 6).

When the difference of product in the two phases is high ($E = -0.5$) Janus particles move along the interface. Interestingly, if the simulations are initialized with different $\theta_p$, particles stabilize at a unique angle, which depends on the particle surface mobility. When the ratio of products in both phases is closer to 1 (e.g. $E = -1/4$), particles continue their motion at interfaces, although they are slower, and a unique angle is no longer observed. For some mobilities, as in $\mu = 0.3$, a single angle is observed, but for others, as for $\mu = 0.5$ we observe the appearance of competing attractors. Thus, both the asymmetric accumulation of the product in both sides and the surface mobility of the particle change the torque the particle feels at the interface and that stabilizes at a certain $\theta_p$.

Finally, in the last scenario where both phases are symmetric with respect to the solute solubility, $E = 0$, particles move very slowly along the interface, and additional attractors for $\theta_p$ appear. Consequently, the asymmetric...
FIG. 3. Motion of an active Janus particle in a single phase fluid. A) Steady state value of the space-averaged increase (with respect to the initial time) of oxygen concentration, \( \langle \phi - \phi_0 \rangle \), as a function of the production rate \( \alpha \) (in lbu), for various degradation rates, \( k_d \). The rest of the data shown in the paper were obtained from simulations with \( \alpha = 10^{-3} \) and \( k_d = 10^{-3} \). B) Particle speed as a function of the phoretic mobility \( \mu_+ \), for different values of \( \mu_- \) (see Eq. (6)), showing a linear dependence as predicted by Eq. (7).

FIG. 4. Equilibrium position, relative to the interface, of an inactive (\( \alpha = 0 \)) particle with uniform phoretic mobility, as a function of \( E \) for various \( \mu \)'s (panel A) and as a function of \( \mu \) for various \( E \)'s (panel B). Data for three different contact angles are shown; particles are initially placed in oil (hydrophobic, \( \theta_c = 0^\circ \)), water (hydrophilic, \( \theta_c = 180^\circ \) or at the interface (neutral, \( \theta_c = 90^\circ \)).

accumulation of product is also responsible for the particles speed at the interface.
FIG. 5. Equilibrium position (panel A) and orientation angle (panel B) relative to the interface of an inactive particle ($\alpha = 0$) with a Janus phoretic mobility profile ($\mu_+ \neq \mu_-$) and neutral wetting ($\theta_c = 90^\circ$) as a function of the rear mobility $\mu_-$, for various values of the front mobility $\mu_+$. The particle, initially placed at the interface with the characteristic vector $\hat{n}$ in the interface plane, tends to escape from the plane by effect of the phoretic repulsion and to rotate due to the mismatching mobilities inducing a torque (in the inset of panel B a typical time evolution of the orientation angle).

FIG. 6. Angle between the particle characteristic vector and the interface, $\theta_p$, as a function of time for an active colloid with $\theta_c = 90^\circ$ (neutral wetting), trapped at the interface. The data sets correspond to various initial orientation angles, two different surface mobilities ($\mu = 0.3$ and $\mu = 0.5$) and to three different oxygen-oil/water affinities: $E = -0.5$ (left panel), $E = -0.25$ (middle panel) and $E = 0$ (right panel). The insets below the curves indicate the progression of the particles along the interface for the case with initial $\theta_p = 60^\circ$ for the $8 \times 10^4$ time steps simulated.

We next analyze the impact of wetting, when a particle is initially placed at the interface and moves along it. We
consider both active and inactive particles and monitor the steady displacement of the particle from the interface plane, at changing the contact angle, the phoretic mobilities and the oxygen solubility parameter. The results are reported in Fig. 4A.

Inactive, non-phoretic ($\mu = 0$) particles are, of course, insensitive to variations of the oxygen field configuration and, hence, to $E$; this is reflected in the full overlap of the data for $E = 0$ (+) and $E = -1/2$ (×). In both cases, though, as expected for passive colloids, the more the contact angle departs from 90°, the further the particle settles away from the interface.

Remarkably, instead, for finite, large enough, phoretic mobility ($\mu = 0.5$), phoretic repulsion is capable to overcome interfacial forces and the particle tends to stay away from the phase richer in oxygen, be it water, $E > 0$ (■), or oil, $E < 0$ (♦), irrespective of its wettability. More precisely, taking, for instance, the case $E < 0$, if phoretic and capillary forces have opposite directions ($\theta_c < 90^\circ$), the particle can be stabilized, roughly, at the interface, but if they have the point towards the same side, the particle leaves the interface plane and there is, basically, no dependence on the contact angle.

Active particles ($\alpha \neq 0$), for which only the case $E < 0$ is shown, manifest a similar behaviour. However, the activity introduces an extra force which has a component normal to the interface (for the steady orientation angle differs, in general, from zero) and pushes the particle closer to the oxygen-rich region. To check if the initial orientation $\theta_p(0)$ plays a role, simulations are run with $\theta_p(0) = 60^\circ$ (■) and $\theta_p(0) = 30^\circ$ (♦). The absence of significant differences indicates that $\theta_p(0)$ does not impact the steady state particle motion. Finally, we study the motion of neutral ($\theta_c = 90^\circ$) active particles that approach the interface from the aqueous phase, when the oxygen is more concentrated in oil ($E < 0$), as displayed in Fig. 4B. We consider both uniform ($\mu_+ = \mu_- = \mu = 0.5$, red) and Janus-like phoretic mobilities ($\mu_+ = 0.5, \mu_- = 0.3$ (black) and $\mu_+ = 0.3, \mu_- = 0.5$ (yellow)).

Janus particles tend to reorient such to minimize the interfacial overlap of the more repulsive side (larger $\mu$) with the solute-rich liquid. Thus, the particle with higher front mobility ($\mu_+ > \mu_-$, in black) faces the water phase (depicted as a blue area in the inset), attaining a value of the orientation angle $\theta_p \approx -90^\circ$, whereas the opposite occurs when $\mu_+ < \mu_-$ ($\theta_p \approx 90^\circ$, in yellow). In both cases, since their director vector $\hat{\eta}$ is orthogonal to the interface and phoretic forces cannot overcome the capillary trapping, they get stuck. On the contrary, for uniform diffusiophoretic mobilities (red particle), interfacial alignment is lacking, and particles displace along the interface.

IV. CONCLUSIONS

In this work we have introduced a new model based on Lattice-Boltzmann to study the interaction of active particles with liquid-liquid interfaces. The model facilitates the study of the full hydrodynamics of the system, on the same footing as diffusiophoretic and wetting forces, suspended particles are subject to. The model allows to switch on and off easily these forces, and to modify the particle properties such as wetting and the diffusiophoretic force, differentiating for this last scenario two parts of the particle with its own activity and mobility. These contributions are formulated locally, and can then be adapted to particles of arbitrary shape, with a general inhomogeneous treatment of their surfaces. Moreover, the liquid mixture can show asymmetric solubility to the chemicals produced by the particles.

We have tested the interaction of inactive particles trapped at the interface under different wetting angles $\theta_c$ (90°, 90° and 180°) and different particle surface mobility. We have seen that while wetting dominates over diffusiophoretic forces, when the wetting is neutral (90°), diffusiophoretic properties are important, and inactive particles with homogeneous surface mobility displace from the interface. This interaction is proportional to the surface mobility, and to the different of products between both phases. When the surface has an asymmetric mobility, particles reorient to have its more repulsive face towards the liquid phase with less product, and displace from the phase of high accumulation of product. The reorientation depends on the strength of the mobility. The more repulsive, the fastest reorient.

Active particles at the interface with neutral wetting move along the interface. The more asymmetry between product accumulation in both phases and the more repulsive is their surface to products, the fastest particles move. Particles reorient themselves to a specific angle, no matter the angle at which particles are placed. However, if the asymmetry of products between both phases decays, particles find different equilibrium positions depending on the initial angle. This effect is seen for different surface mobilities. If wetting is changed, particles will stay closer to the interface rather if they would not have the activity. If particles with high wetting for the side of initial motion move towards the interface, they will contact the interface, reorient and move along the interface. Depending on the ratio of the surface mobilities, particles can stop, or continue their motion.

Overall, the proposed model has huge capabilities to explain many phenomena occurring at these interfaces, and that sets a new start line where to study these and more complex systems.

ACKNOWLEDGMENTS

L.P. would like to thank MINECO for the FPI BES-2016-077705 fellowship. A.S. acknowledges support
FIG. 7. A) Steady particle displacement with respect to the interface as a function of the contact angle, for various combinations of $\mu$, $E$ and $\alpha = 0$ (inactive) or $\alpha = 10^{-3}$ (active). In the active case, data for two different values of the initial orientation angle are shown: $\theta_p(0) = 30^\circ$ (■) and $\theta_p(0) = 60^\circ$ (○). B) Trajectory (in a plane orthogonal to the interface) of an active particle initially placed in water and oriented towards the interface (indicated with the dashed line); the initial orientation angle is $\theta = 30^\circ$ and the colloid is neutral ($\theta_c = 90^\circ$). Three combinations of phoretic mobilities, ($\mu_+, \mu_-$), are considered: (0.5, 0.5) (red), (0.5, 0.3) (blue) and (0.3, 0.5) (green).

from the European Research Council under the European Union Horizon 2020 Framework Programme (No. FP/2014-2020), ERC Grant Agreement No. 739964 (COPMAT). I.P. acknowledges support from Ministerio de Ciencia, Innovación y Universidades (Grant No. PGC2018-098373-B-100/FEDER-EU), DURSI (Grant No. 2017 SGR 884), SNSF (Project No. 200020_16471), and EU Horizon 2020 Program (Grant FET-OPEN 766972-NANOPHLOW).

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

[1] S. Sánchez, L. Soler, and J. Katuri, Angew. Chem. Int. Ed. 54, 1414 (2015).
[2] S. Ramaswamy, Annu. Rev. Condens. Matter Phys. 1, 323 (2010).
[3] J. L. Anderson, Annu. Rev. Fluid Mech. 21, 61 (1989).
[4] W. Paxton, K. Kistler, C. Olmeda, A. Sen, S. St. Angelo, Y. Cao, T. Mallouk, P. Lammert, and V. Crespi, J. Am. Chem. Soc. 126, 13424 (2004).
[5] J. Howse, R. Jones, A. Ryan, T. Gough, R. Vafabakhsh, and R. Golestanian, Phys. Rev. Lett. 99, 048102 (2007).
[6] I. Theurkauff, C. Cottin-Bizonne, J. Palacci, C. Ybert, and Bocquet, Phys. Rev. Lett. 108, 268303 (2012).
[7] G. Volpe, I. Buttinoni, D. Vogt, H.-J. Kümmerer, and C. Bechinger, Soft Matter 7, 8810 (2011).
[8] J. Palacci, S. Sacanna, A. Steinberg, D. Pine, and P. Chaikin, Science 339, 936 (2013).
[9] W. Paxton, S. Sundararajan, T. Mallouk, and A. Sen, Angew. Chem. Int. Ed 45, 5420 (2006).
[10] S. Ebbens and J. Howse, Soft Matter 6, 726 (2010).

[11] C. Bechinger, R. Di Leonardo, H. Löwen, C. Reichhardt, G. Volpe, and G. Volpe, Rev. Mod. Phys. 88, 045006 (2016).
[12] I. Buttinoni, J. Bialké, F. Kümmerel, H. Löwen, C. Bechinger, and T. Speck, Phys. Rev. Lett. 110, 238301 (2013).
[13] R. Golestanian, Phys. Rev. Lett. 108, 038303 (2012).
[14] M. Yang, A. Wysocki, and M. Ripoll, Soft Matter 10, 6208 (2014).
[15] J. Simmchen, J. Katuri, W. E. Uspal, M. N. Popescu, M. Tasinkevych, and S. Sánchez, Nat. Commun. 7, 10598 (2016).
[16] J. Katuri, D. Caballero, R. Voituriez, J. Samitier, and S. Sanchez, ACS Nano 12, 7282 (2018).
[17] W. E. Uspal, M. N. Popescu, S. Dietrich, and M. Tasinkevych, Soft Matter 11, 434 (2015).
[18] A. Domínguez, P. Malgaretti, M. N. Popescu, and S. Dietrich, Phys. Rev. Lett. 116, 078301 (2016).
[19] P. Malgaretti, M. N. Popescu, and S. Dietrich, *Soft Matter* **12**, 4007 (2016).
[20] X. Wang, M. In, C. Blanc, P. Malgaretti, M. Nobili, and A. Stocco, *Faraday Discuss.* **191**, 305 (2016).
[21] T. Peter, P. Malgaretti, N. Rivas, A. Scagliarini, J. Harting, and S. Dietrich, *Soft Matter* **16**, 3536 (2020).
[22] L. S. Palacios, J. Katuri, I. Pagonabarraga, and S. Sánchez, *Soft Matter* **15**, 6581 (2019).
[23] R. Benzi, S. Succi, and M. Vergassola, *Phys. Rep.* **222**, 145 (1992).
[24] D. Wolf-Gladrow, *Lattice-gas cellular automata and lattice Boltzmann models: an introduction*, edited by Springer (2000).
[25] T. Krüger, H. Kusumaatmaja, A. Kuzmin, O. Shardt, G. Silva, and E. Viggen, *The lattice Boltzmann method*, edited by Springer (2017).
[26] M. R. Swift, E. Orlandini, W. R. Osborn, and J. M. Yeomans, *Phys. Rev. E* **54**, 5041 (1996).
[27] V. Kendon, M. Cates, I. Pagonabarraga, J.-C. Desplat, and P. Bladon, *J. Fluid Mech.* **440**, 147 (2001).
[28] L. Carenza, G. Gonnella, A. Lamura, G. Negro, and A. Tiribocchi, *Eur. Phys. J. E* **42**, 81 (2019).
[29] A. Scagliarini and I. Pagonabarraga, *Soft Matter* **16**, 8893 (2020).
[30] A. J. C. Ladd, *J. Fluid Mech.* **271**, 285 (1994).
[31] A. J. C. Ladd, *J. Fluid Mech.* **271**, 311 (1994).
[32] N.-Q. Nguyen and A. J. C. Ladd, *Phys. Rev. E* **66**, 046708 (2002).
[33] C. Aidun, Y. Lu, and E.-J. Ding, *J. Fluid Mech.* **373**, 287 (1999).
[34] R. Golestanian, T. B. Liverpool, and A. Ajdari, *New J. Phys.* **9**, 126 (2007).
[35] R. Golestanian, T. B. Liverpool, and A. Ajdari, *Phys. Rev. Lett.* **94**, 220801 (2005).
[36] M. Popescu, S. Dietrich, M. Tasinkevych, and J. Ralston, *Eur. Phys. J. E* **31**, 351 (2010).
[37] J.-C. Desplat, I. Pagonabarraga, and P. Bladon, *Comp. Phys. Commun.* **134**, 273 (2001).
[38] J. Joanny and P. de Gennes, *J. Chem. Phys.* **81**, 552 (1984).