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Phoretic motion of soft vesicles and droplets: an XFEM/particle-based numerical solution

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Abstract

When immersed in solution, surface-active particles interact with solute molecules and migrate along gradients of solute concentration. Depending on the conditions, this phenomenon could arise from either diffusiophoresis or the Marangoni effect, both of which involve strong interactions between the fluid and the particle surface. We introduce here a numerical approach that can accurately capture these interactions, and thus provide an efficient tool to understand and characterize the phoresis of soft particles. The model is based on a combination of the extended finite element—that enable the consideration of various discontinuities across the particle surface—and the particle-based moving interface method—that is used to measure and update the interface deformation in time. In addition to validating the approach with analytical solutions, the model is used to study the motion of deformable vesicles in solutions with spatial variations in both solute concentration and temperature.

Keywords

Phoretic motion; Diffusiophoresis; Marangoni effect; Droplets; Extended finite element method

1 Introduction

The self-propulsion of micro and nano-particles has recently caught much attention as a new direction in active nano-systems for drug delivery [1], self-healing materials [2] and micro-robotics [3]. Self-propelled particles indeed have the potential to carry cargo, target specific locations and release material within confined spaces of porous media (such as biological materials). Among the numerous strategies for self-propulsion, the design of particles that takes the advantage of the interactions between their surface and the surrounding solution has gained much attention due to their versatility and easiness for implementation. One such example is the Janus particle [4], which achieves motion by utilizing an asymmetry in chemical interaction between its front and back to generate an effective thrust along the direction of concentration gradient. Symmetrical vesicles can also respond to chemical and temperature gradients via the so-called Marangoni effect, where the surrounding fluid locally alter the vesicle's surface tension to produce a driving force for its locomotion [5]. When the Marangoni effect is inactive, another phenomenon, called “diffusiophoresis” can

also take over [6–8]. In this situation, surface-solute interactions in a nanometer-thin layer around the particle surface produce an active flow that eventually leads to directed motion. This mechanism is however preferred for solid particles since the traditional Laplace law for fluid interfaces does not apply. From a theoretical standpoint, this class of problem has first been addressed in the 1940's by Derjaguin [6] and more rigorously studied in 1980's, notably with the work of Anderson [9] with the use of continuum approaches. In the process of deriving an analytical solution for the resultant velocity of a migrating particle, Anderson found that the driving force for its motion was affected by the competition between two mechanisms: fluid convection and solute diffusion [10,11] whose relative contributions are dictated by the Peclet number [12,13]. While a number of theoretical predictions could be made regarding the velocity of self-or externally driven particle motion, several limitations still hinder further works. For instance, analytical approaches are often restricted to simple and rigid particle geometries, symmetrical shapes and ideal boundary conditions. This precludes studies of important problems such as coupled particle motion and deformation [14], particle motion in a complex fluid field [15], multiple particles interactions [16] and the interaction between particle and boundaries [17]. Numerical methods provide a perfect avenue to address these shortcomings but have so far focused on rigid particles [18,19] or the local interactions on the surface of a soft vesicle [20]. The phoretic motion of vesicles can be generally cast as fluid-structure interaction problem, for which a number of numerical strategies have been proposed. These include for instance the boundary-fitted methods [21], the immersed boundary method [22–24], the immersed finite element method [25–27] or the distributed Lagrange Multiplier method/fictitious domain methods [28,29] for which the interactions between the fluid and the solid are materialized with fictitious forces distributed in the overlapping regions or boundary of the fluid-solid domains. The Boundary Integral (BI) method and the coupled lagrange-eulerian method [30] that describe the kinetics of moving interfaces have also been successful in dealing with multiphase flow problems within the regime of potential flows or Stokes flows [31,32]. They however do not consider discontinuities in fluid flow across the interface. Although the no-slip boundary condition is widely imposed and justified in the study of fluid-solid interface problems at macroscopic scales, it may not be valid at the microscopic scale [33]. In fact, the violation of the no-slip boundary condition has been reported experimentally, notably in micro-fluidic experiments involving fluid flows through thin lyophobic capillaries [34], in micro channels [35], hydrophobic surfaces and hydrophilic surfaces under some specific conditions [36]. Thus, in order to fully describe problems that involve interactions between a fluid and a substrate at microscopic scales, it is essential to account for a slip boundary condition. More specifically, for the problem of phoretic motion of vesicles, the principal driving mechanism is the existence of an active slip flow on the vesicle surface. While this phenomenon has been explored with analytical approaches [9,13], there has not been, to the best of our knowledge, related computational studies. The behavior of these systems in complex conditions (boundary conditions, geometry and physical properties) therefore remains elusive from a modelling standpoint.

In the present paper, we propose a numerical method based on the extended finite element method (XFEM) and particle-based moving interface method (PMIM) [37,38] that can naturally describe the generation of active flow on particle surfaces and its mobility. The X-

FEM is indeed ideal to model a variety of problems [39–43] where field discontinuities play an important role. The PMIM further provides a flexible complementary method when boundaries move on the background mesh [37]. The proposed approach possesses three main features that are particularly important in the context of particle propulsion: (a) First, the discontinuous tangential velocity and pressure caused by the phoretic active flow is accounted by introducing enriched tangential degrees of freedom for the fluid velocity across the interface. (b) The kinematics and changes in curvature of the interface, that are key players in the particle's equilibrium, are naturally tracked by a set of numerical particles along the interface. (c) The method is flexible and can be adapted to investigate more complicated systems exhibiting elastic properties, or comprising multiple particles or particle-boundary interactions. The manuscript is organized as follows. In Sect. 2, we introduce the mathematical formulation that describes the mechanical and chemical interactions between a soft vesicle and an external solution. In Sect. 3, the PMIM/XFEM numerical solution procedure is introduced for the specific problem of particle phoresis. In Sect. 4, we first investigate the convergence and accuracy of numerical solutions by comparing them with well-known analytical solutions. A few numerical examples predicting the migration and deformation of vesicles under concentration and temperature gradients are then shown. Section 5 finally provides a short discussion and concluding remarks.

2 Mathematical formulation for an active vesicle immersed in fluid

In this work, we consider an impermeable and deformable vesicle whose boundary is defined by the closed interface Γ immersed in an axisymmetric fluid domain Ω as shown in Fig. 1. The fluid domain can further be divided into two sub-domains Ω^+ and Ω^- , denoting volumes outside and inside the vesicle, respectively. In the remainder of this paper, we associate any field existing in Ω^+ with a superscript $+$, while a subscript $-$ is used for fields inside the vesicle (Ω^-). For simplicity, the two fluids are considered incompressible and Newtonian with viscosities μ^+ and μ^- in their corresponding domains. The external fluid in Ω^+ is moreover assumed to contain a small amount of diluted solute molecules whose concentration c can vary spatially. The vesicle's behavior is finally governed by two factors: its surface tension γ and the reactivity of its surface with the solution as discussed later in this section.

2.1 Notations

To quantify the behavior of this system, it is first important to introduce a set of notations and operators that can characterize the physical state of a solution (fluid and solute) near the vesicle. An incompressible solution can generally be described by its velocity $\mathbf{v}(\mathbf{x}, t)$, pressure $p(\mathbf{x}, t)$ and solute concentration (or temperature) $c(\mathbf{x}, t)$ where $\mathbf{x}$ is the coordinate of an eulerian point in a predefined cartesian coordinate system and t denotes the time from a known initial state. Similarly, a point on the interface Γ is described by its velocity $\bar{\mathbf{v}}(\mathbf{x}, t)$ that does not need to be the same as that of the fluid. To understand these differences, it is convenient to split the fluid velocity on Γ into its normal ($\mathbf{v}^\perp$) and tangential ($\mathbf{v}^\parallel$) projections such that:

$$\mathbf{v} = \mathbf{v}^\perp + \mathbf{v}^\parallel \quad (1)$$

where $\mathbf{v}^\perp = [\bar{\mathbf{n}} \otimes \bar{\mathbf{n}}] \mathbf{v}$ and $\mathbf{v}^\parallel = [\mathbf{I} - \bar{\mathbf{n}} \otimes \bar{\mathbf{n}}] \mathbf{v}$ 44 Here, $\bar{\mathbf{n}}$ denotes the normal vector to the interface and $\mathbf{I}$ is the second-order identity tensor. As discussed later, the interactions between the vesicle's interface and the solute can, in certain cases, create discontinuities in otherwise continuous fields across Γ . For instance, although for an impermeable interface, the normal velocity of the interface is equal to that of the surrounding fluid (i.e. $\bar{\mathbf{v}}^\perp = \mathbf{v}^\perp = \bar{\mathbf{v}}^\perp$ [45]), we will see that discontinuities in tangential velocities $[\mathbf{v}]^\parallel$ can exist on both side of the vesicle's surface. These will be represented by:

$$[\mathbf{v}]^\parallel = \bar{\mathbf{v}}^\parallel - \mathbf{v}^\parallel \quad \text{and} \quad [\mathbf{v}]^\parallel = \mathbf{v}^\parallel - \bar{\mathbf{v}}^\parallel \quad (2)$$

Similarly, jumps in solute concentration (or temperature) and fluid pressure across Γ are expressed by:

$$[c] = c^+ - c^- \quad \text{and} \quad [p] = p^+ - p^- \quad (3)$$

2.2 Governing equations

At low Reynolds numbers, the system is described by Stokes's equation for the fluid and the classical convection-diffusion equation for the solute. For the problem of vesicle phoresis, however, these must be complemented by interface constitutive relations that represent the fine scale interactions between the solute and the vesicle's surface. In this work, we particularly concentrate on the response of a vesicle to spatial variations in either chemical concentrations or temperature, both of which will be represented by a generic scalar field $c(\mathbf{x}, t)$.

Convection–diffusion in the fluid medium—Due to the small length-scales and velocities associated with our problem, the Reynolds number is relatively low (i.e. $Re \ll 1$) and one can limit ourselves to the regime of incompressible stokes flow. This is described by the coupled differential equations for the Cauchy stress $\boldsymbol{\sigma}$ and velocity $\mathbf{v}$ as:

$$\nabla \cdot \boldsymbol{\sigma} = 0 \quad \text{with} \quad \boldsymbol{\sigma} = \mu \mathbf{D} - p \mathbf{I} \quad \nabla \cdot \mathbf{v} = 0 \quad (4)$$

where $\mathbf{D} = (\nabla \mathbf{v})^s$ is the symmetric part of the velocity gradient. The distribution of solute molecules (or temperature) is then described by a transport equation that contains both convective and diffusive effects in the form:

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = D \nabla^2 c \quad (5)$$

where D is the diffusion coefficient (or, respectively the conductivity for the thermal problem) in the fluid and ∇^2 is the Laplacian operator.

Fluid-interface interactions—As discussed in [37], the force equilibrium for a fluid-fluid interface can generally be written in terms of the jump in the stress vector across Γ as:

$$[\boldsymbol{\sigma} \cdot \bar{\mathbf{n}}] = -2\gamma\mathcal{H}\bar{\mathbf{n}} \quad (6)$$

with $\mathcal{H}$ the mean curvature of the interface and γ its surface tension. The normal projection of this equation yields the standard Laplace–Young relation [46]:

$$[p] = -2\gamma\mathcal{H} \quad (7)$$

while the tangential projection implies that the tangential stress vector $(\boldsymbol{\sigma} \cdot \bar{\mathbf{n}})^{\parallel}$ is continuous across the interface. Equation (6) is furthermore complemented with the tangential force balance between the membrane and the interface [37], or Navier condition that reads:

$$(\boldsymbol{\sigma} \cdot \bar{\mathbf{n}})^{\parallel+} = \left(\frac{\mu}{\ell}\right)^+ \{[\mathbf{v}]^{\parallel+} - \mathbf{v}_a\} \quad (8)$$

$$(\boldsymbol{\sigma} \cdot \bar{\mathbf{n}})^{\parallel-} = \left(\frac{\mu}{\ell}\right)^- [\mathbf{v}]^{\parallel-} \quad (9)$$

where $\ell > 0$ are the slip length parameters enforced on the convective flow (on each side of Γ); the case $\ell = 0$ corresponds to a no-slip condition while $\ell = \infty$ corresponds to a free-slip condition at the interface. The quantity $\mathbf{v}_a$ is the active tangential velocities created by the solute-interface interactions, the source of which will be discussed later in this section. Note that the term $[\mathbf{v}]^{\parallel+} - \mathbf{v}_a$ can also be written $(\bar{\mathbf{v}}^{\parallel} - \mathbf{v}_a) - \mathbf{v}^{\parallel+}$. In other words, the slip length ℓ measures the velocity discontinuity between the external solution and the active surface flow on the vesicle surface. To complete the interface description, one should finally enforce the conservation laws on the interfacial layer. For a solution, this takes the form of the mass conservation of the solute, while for a heated fluid, this becomes the conservation of energy. Following the analysis described in [45], we find that:

$$\nabla_s \cdot (\mathbf{q}^{\parallel}) = \frac{1}{K} [\mathbf{q}^{\perp}] \quad (10)$$

where K is the effective thickness of the interfacial layer (Fig. 2). In the above equation, the first term represents the surface divergence of the tangential flux $\mathbf{q}^{\parallel}$ of solute (or heat flux, respectively) while the second indicates the discontinuity in normal flux of solute (or heat

flux, respectively) in the bulk and in the interface. Using linear constitutive relations for the interface transport problem, the normal and tangential flux may further be decomposed as:

$$\mathbf{q}_+^\perp = (-D\bar{\mathbf{n}} \cdot \nabla c)^+, \quad \mathbf{q}_-^\perp = \kappa [c]$$

$$\mathbf{q}^\parallel = -D\nabla_s c + c\mathbf{v}_a \quad (11)$$

where κ is to be interpreted as the normal permittance of the interface to either solute molecules or heat, depending on the problem.

2.3 Phoretic motion: constitutive relations

In this work, we consider two types of interactions occurring at the interface between the fluid medium and the vesicle. The first, denoted as Diffusiophoresis, generates an active flow on the vesicle surface that is proportional to the thickness of interfacial layer. The second, known as the Marangoni effect, affects the local surface energy of the vesicle resulting in variations in its surface tension. This results in an effective and size-dependent vesicle velocity. Since the size of vesicle is about three orders of magnitude greater than the thickness of the interfacial layer, the characteristic velocity from the diffusiophoretic mechanisms is typically much smaller than that triggered by the Marangoni effect [9]. For a micro-vesicle, the Marangoni effect is therefore dominant while for rigid particle, the former vanishes and diffusiophoresis becomes the main contributor to particle motion.

Diffusiophoresis—During diffusiophoresis, the vesicle surface interacts with solute particles via van der Waals and dipole interactions. At the nano-scale, these interactions materialize in the form of a force field $f(y)$ between the surface and solute particles located at a distance y from it. The dependency of this force on distance can conveniently be expressed in terms of a potential $\Phi(y)$ such that the interaction force is $f = -\Phi'/y$. The presence of this force affects the stress state in the fluid such that if the solute concentration varies along the interface, the resulting stress gradient triggers a tangential flow within a few nanometer thick interfacial layer (Fig. 2a).

Since the interfacial layer is small compared to the vesicle radius R , it is reasonable to use the active fluid velocity at the outer edge of the interfacial layer as the resultant active flow velocity $\mathbf{v}_a$. Anderson and Prieve [47] solved the Stokes equation within the interfacial layer to find that:

$$\mathbf{v}_a = M\nabla_s c \quad \text{where} \quad M = -\frac{k_B T}{\mu} K L^* \quad (12)$$

where $\nabla_s = (\mathbf{I} - \mathbf{nn})\nabla$ is the tangential gradient operator and $k_B T$ the thermal energy. The mobility coefficient M [12] depends on the effective thickness K and the first moment of the solute distribution L , both expressed in terms of the potential Φ as:

$$K = \int_0^\infty [\exp(-\Phi(y)/k_B T) - 1] dy \quad (13)$$

$$L = K^{-1} \int_0^\infty y [\exp(-\Phi(y)/k_B T) - 1] dy \quad (14)$$

These quantities represent the type of solute-interface interaction (adsorption/emission) and eventually dictate whether the sign of the mobility coefficient. Finally, considering that the vesicle is impermeable to solute ($\kappa = 0$), substituting (11) into (10) leads us to the final expression of the mass balance of solute in the interfacial layer:

$$-(D\bar{\mathbf{n}} \cdot \nabla c)^+ = K \nabla_s \cdot (-D \nabla_s c + c \mathbf{v}_a) \quad (15)$$

This equation shows that the flux of solute onto the interface (first term) is propagated into the interfacial layer either by diffusion processes (second term) or by convective processes (third term) [47,48].

Marangoni effect—For fluid vesicles and droplets, the discontinuous pressure at the interface generated by surface tension can also contribute to self-propulsion. This capillary-driven flow can result from different sources including a gradient of solute concentration [49], temperature [5] or electric field [50]. Here, to be general, we use the temperature induce Marangoni effect as example, although the formulation works equally well for solute concentration. When a fluid vesicle is placed in a fluid that displays variations in temperature, its surface tension changes because the intermolecular hydrogen bonding is reduced by the increase in temperature. The pole of the vesicle interacting with the highest temperature experiences the lowest surface tension. This phenomenon breaks the droplet's symmetry whereby the area of higher surface tension tends to contract while the opposite end tends to expand. The variation of surface tension along Γ can indeed be related to temperature gradient by using the chain rule:

$$\nabla_s \gamma = \frac{\partial \gamma}{\partial c} \nabla_s c \quad (16)$$

This relation, together with (7), can be used to express the variation in pressure difference across the interface as follows:

$$\nabla_s [p] = -2 \nabla_s (\gamma \mathcal{H}) = -2 \mathcal{H} \frac{\partial \gamma}{\partial c} \nabla_s c - 2 \gamma \nabla_s \mathcal{H} \quad (17)$$

The above quantity can be thought of as a driving force that propels the vesicle towards areas of higher temperature. This force arises from two contributions: (a) a variation in temperature and (b) a variation of the mean curvature $\mathcal{H}$ of the interface. Note that for a

spherical particle, the second term vanishes and we obtain $\nabla_s [p] = 2\mathcal{H}\gamma' \nabla_s c$, where $\gamma' = \gamma/c$ is the thermal-coefficient of surface energy. Moreover, different from diffusiophoresis, there is no active flow generated on the surface and the interfacial layer vanishes. In this case, Eq. (17) is complemented by the energy conservation in the interface. Denoting the effective thickness K as the thickness of the interface (Fig. 2b), Eq. (11) should be modified as follows:

$$\mathbf{q}_+^\perp = (-D\bar{\mathbf{n}} \cdot \nabla c)^+, \quad \mathbf{q}_-^\perp = \kappa [c]$$

$$\mathbf{q}^\parallel = -D_I \nabla_s c \quad (18)$$

with $\kappa = -D_I/K$ and D_I are respectively the thermal permittance and the conductivity of interface. With these expressions, the conservation of energy on the interface can be written from Eq. (10) as:

$$-(D\bar{\mathbf{n}} \cdot \nabla c)^+ = -K D_I \nabla_s^2 c + \kappa [c] \quad (19)$$

2.4 Non-dimensionalization and boundary conditions

For the sake of simplicity, let us first non-dimensionalize our system in order to better understand its intrinsic response. This operation will enable us to generally understand how particle motion scales relatively to changes in the properties including the characteristic flow velocity ($V = M\bar{V}c_\infty$), the fluid viscosity μ_w , the vesicle radius R and the solute concentration c_∞ in the far field. The non-dimensionalized time, velocity, stress and concentration (or temperature) are then:

$$t^* = \frac{t}{V} R, \quad \mathbf{v}^* = \frac{\mathbf{v}}{V}, \quad \boldsymbol{\sigma}^* = \frac{R}{\mu_w V} \boldsymbol{\sigma}, \quad c^* = \frac{c}{c_\infty} \quad (20)$$

while the gradient operator becomes $\nabla^* = R\nabla$. The new non-dimensionalized unknowns of the system are therefore the normalized fluid velocity $\mathbf{v}^*$, fluid pressure p^* , and solute concentration (or temperature) c^* in the fluid domain Ω . On the interface, they are the normalized tangential interface velocity $\bar{\mathbf{v}}^*$, pressure jump $[p^*]$ and concentration (or temperature) discontinuity $[c^*]$ across Γ . The tangential motion of the interface is furthermore captured by the three velocities $\{\bar{\mathbf{v}}^*, \mathbf{v}^{*\parallel+}, \mathbf{v}^{*\parallel-}\}$ or alternatively, the triplet $\{\bar{\mathbf{v}}^*, \mathbf{v}^{*\parallel+}, [\mathbf{v}]^{*\parallel}\}$. Within this framework, governing equations (4) and (5) are rewritten:

$$r^\pm \nabla^{*2} \mathbf{v}^* - \nabla^* p^* \mathbf{I} = 0 \quad (21)$$

$$\nabla \cdot \mathbf{v}^* = 0 \quad (22)$$

$$|Pe| \left(\frac{\partial c^*}{\partial t^*} + \mathbf{v}^* \cdot \nabla^* c^* \right) - \nabla^{*2} c^* = 0 \quad (23)$$

and the interface Eqs. (7), (8), (9) and (10) become:

$$2\gamma^* \mathcal{H} - [p^*] = 0 \quad (24)$$

$$(\boldsymbol{\sigma}^* \cdot \bar{\mathbf{n}})^\pm - \frac{r^\pm}{\ell^{*\pm}} \{ [\mathbf{v}^*]^\pm - \mathbf{v}_a^{*\pm} \} = 0 \quad (25)$$

$$(-\bar{\mathbf{n}} \cdot \nabla^* c^*) + K^* \nabla_s^* \cdot \mathbf{q}^\parallel - \frac{1}{K^*} [c^*] = 0 \quad (26)$$

where $r^\pm = \mu^\pm / \mu_w$ is the ratio between the kinetic viscosities $\mu^\pm$, $K^* = K/R$ the nondimensional effective thickness, $\mathbf{q}^\parallel = -D_r \nabla_s^* c^* + |Pe| c^* \mathbf{v}_a^*$ the nondimensional tangential flux, where $D_r = D_f/D$ the ratio between the diffusivity of the interface and fluid. These equations are complemented by initial and boundary conditions that will be provided in numerical examples in Sect. 4.

3 Numerical Solution

The objective of this section is to derive an Extended Finite Element (XFEM) solution strategy for solving the above set of equations on a fixed Eulerian mesh. The moving interface Γ is then described independently from this mesh via a set of particles whose position are updated in time using the particle-based moving interface method (PMIM) algorithm discussed in [37]. For the sake of clarity, we omit the superscript '*' for the non-dimensionalized variables in the remainder of the manuscript.

3.1 Extended finite element method for Eulerian fields

We here describe the derivation of the XFEM discretization of the governing equations (21–26). In the numerical solution, we solve the Stokes equations for $\mathbf{v}$, p and $\bar{v}^\parallel$, as well as the convection-diffusion for c . On the interface, the Lagrange multiplier method is implemented to enforce the interface Eqs. (24–26). More specifically, in addition to the existing unknowns, we also solve for λ_p that enforces the discontinuous pressure (24), λ^+ and λ^- for discontinuous tangential velocity (25) at the outer and inner side of the interface, respectively, and λ_c for the discontinuous solute concentration (or temperature) (26).

Weak form—To construct the weak form of our problem, we first introduce a set of arbitrary test functions ω_v and $\omega_{\bar{v}}$ in $\mathcal{V}$, ω_p in $\mathcal{P}$, ω_c in $\mathcal{C}$, as well as ω_{λ_p} , ω_{λ^-} and ω_{λ_c} in $\mathcal{L}$, where $\mathcal{V}$, $\mathcal{P}$, $\mathcal{C}$ and $\mathcal{L}$ are the admissible spaces for velocity, pressure, concentration (or temperature) and Lagrange Multiplier, respectively. Multiplying the governing equations (21–26) with their corresponding test functions and integrating over the numerical domain Ω , the problem can be cast as follows: find the fields $\mathbf{v}$, p , c in the bulk, and $\bar{v}$, λ_p , λ^+ , λ^- , λ_c on the interface such that for all functions ω_v , ω_p , ω_c , $\omega_{\bar{v}}$, ω_{λ_p} , ω_{λ^+} , ω_{λ^-} and ω_{λ_c} , the following integral equations are satisfied in Ω and on Γ associated with Eqs. (21–23):

$$(\nabla \omega_v, r \nabla \mathbf{v})_{\Omega} - (\nabla \omega_v, p \mathbf{I})_{\Omega} + \left(\omega_v, \frac{r^+}{l^+} \lambda^+ - \frac{r^-}{l^-} \lambda^- \right)_{\Gamma} + (\omega_v, \bar{\mathbf{f}}) = 0$$

$$(\omega_p, \nabla \cdot \mathbf{v})_{\Omega} - (\omega_p, \lambda_p)_{\Gamma} = 0$$

$$(\omega_c, |Pe| \dot{c})_{\Omega} + (\omega_c, |Pe| \mathbf{u} \cdot \nabla c)_{\Omega} + (\nabla \omega_c, \nabla c)_{\Omega} + (\omega_c, \lambda_c)_{\Gamma} = 0 \quad (27)$$

and the following equations associated with Eqs. (24–26):

$$\left(\omega_{\bar{v}}, \frac{r^+}{l^+} [\mathbf{v}]^{\parallel+} - \mathbf{v}_a + \lambda^+ \right)_{\Gamma} + \left(\omega_{\bar{v}}, \frac{r^-}{l^-} [\mathbf{v}]^{\parallel-} - \lambda^- \right)_{\Gamma} = 0$$

$$(\omega_{\lambda_p}, [p] - 2\gamma \mathcal{H})_{\Gamma} = 0$$

$$\left(\omega_{\lambda^+}, [\sigma \cdot \bar{\mathbf{n}}]^{\parallel+} - \frac{\mu}{l^+} [\mathbf{v}]^{\parallel+} + \mathbf{v}_a \right)_{\Gamma} = 0$$

$$\left(\omega_{\lambda^-}, [\sigma \cdot \bar{\mathbf{n}}]^{\parallel-} - \frac{\mu}{l^-} [\mathbf{v}]^{\parallel-} \right)_{\Gamma} = 0$$

$$\left(\omega_{\lambda_c}, (-\bar{\mathbf{n}} \cdot \nabla c)^+ + K \nabla_s \cdot \mathbf{q}^{\parallel} + [c] / K \right)_{\Gamma} = 0 \quad (28)$$

where the notation $(\cdot, \cdot)_{\Omega}$ corresponds to the L^2 inner product with respect to the Ω domain. We note that the fields $\mathbf{v}$, p , c are continuous in Ω^+ and Ω^- , while discontinuous across Γ , and the fields $\bar{v}$, λ_p , λ^+ , λ^- , λ_c are continuous on Γ .

XFEM interpolation—Although the diffusiophoresis problem is three dimensional (3D), only 2-D discretization is required to solve the problem due to its axial-symmetry. Following the classical solution strategy for Stokes flow and solute convection diffusion, the pressure, concentration and velocity fields are discretized in a 2-D fixed finite element mesh and interpolated in a mixed fashion with 4-nodes bilinear shape function for the pressure and concentration fields and 9-nodes quadratic shape functions for the velocity field [37]. Due to the Eulerian nature of the governing equations, the mesh is structured and does not conform with the shape of vesicle interface Γ . The interface is then represented by the zero-level of a levelset function $\phi(\mathbf{x})$ defined as the signed distance function from Γ [37]. For an element that is cut by the interface, special interpolation functions [51,52] are therefore required to capture discontinuous field across Γ (Fig. 3). The pressure and concentration or temperature fields (represented by the symbol f for generality) in an element e are thus approximated by:

$$f(\mathbf{x}, t) = \sum_{I=1}^4 N_4^I(\mathbf{x}) f^I(t) + \sum_{I=1}^4 N_4^I(\mathbf{x}) (H(\phi(\mathbf{x})) - H(\phi(\mathbf{x}^I))) \hat{f}^I(t)$$

where I is the local node number that ranges from 1 to 4 for bilinear shape functions N_4 . The quantity f^I represents the nodal value of the function f while enriched nodal freedom $\hat{f}^I$ is used to describe the discontinuity across Γ as interpolated with the Heaviside function $H(\phi(\mathbf{x}))$. The strategy for the enrichment of velocity field $\mathbf{v}$ is more complicated since only the tangential component is discontinuous. This can however be done by projecting the velocity on the tangent vector $\mathbf{a}^I$ to the interface at node I as follows:

$$\mathbf{v}(\mathbf{x}, t) = \sum_{I=1}^9 N_9^I(\mathbf{x}) \mathbf{v}^I(t) + \sum_{I=1}^9 N_9^I(\mathbf{x}) (H(\phi(\mathbf{x})) - H(\phi(\mathbf{x}^I))) \hat{v}^{\parallel I}(t) \mathbf{a}^I$$

where the N_9 is the 2-D quadratic shape function and $\hat{v}_i^{\parallel I}$ is the enriched velocity unknown at node I . Finally, the Lagrange multipliers λ_p , λ^+ , λ^- , λ_c and the tangential interface velocity $\bar{v}^{\parallel}$ are interpolated along the interface section Γ^e cut by element e as follows:

$$\bar{f}(\mathbf{x}, t) = \sum_{I=1}^2 \bar{N}^I(\mathbf{x}, t) \bar{f}^I(t)$$

where $\bar{N}$ is 1-D linear shape function and $\bar{f}$ is a scalar field defined on the interface. We note here that special treatments are necessary along the interface for the solution to be stable and avoid ill-conditioned matrices. Readers may refer to the work of Moes et al. [53] and Sauerland et al. [54] for numerical strategies that address these issue.

Discretized weak form and XFEM equations—To obtain a compact version of the discretized equations, the interpolated fields are written in a vector form as:

$$\tilde{f}^e(\mathbf{x}, t) = \mathbf{N}^4(x) \cdot \mathbf{f}^e(t) \quad (29)$$

$$\tilde{\mathbf{v}}^e(\mathbf{x}, t) = \mathbf{N}^9(x) \cdot \mathbf{v}^e(t) \quad (30)$$

where, again, the field f is used to denote either pressure, concentration or temperature and is expressed by its nodal values $\mathbf{f}^e(t) = \{f^1 \dots f^4, \hat{f}^1 \dots \hat{f}^4\}^T$. The nodal velocities are similarly expressed by $\mathbf{v}^e(t) = \{v_x^1, v_y^1, \dots, v_x^9, v_y^9, \hat{v}^1, \dots, \hat{v}^9\}^T$ in which $\hat{f}^I$ and $\hat{v}^I$ represent the enriched degrees of freedom. Degrees of freedom associated with the interface are also written in the form:

$$\tilde{f}(\mathbf{x}, t) = \overline{\mathbf{N}}(\mathbf{x}) \cdot \overline{\mathbf{f}}^e(t) \quad (31)$$

Here the vector $\overline{\mathbf{f}}$ stands for either the magnitude of the tangential interface velocity $\overline{v}_{\parallel}$ or the Lagrange multipliers λ_p , $\lambda^\pm$ and λ_c (the detailed expressions and derivatives of the shape functions can be found in “Appendix 1”). Using these interpolations into the weak form and after further simplifications (see “Appendix 2”), the discretized governing equations take the following matrix form:

$$\begin{bmatrix} \mathbf{K}^T & \mathbf{I}_2^T \\ \mathbf{I}_1^T & \overline{\mathbf{K}}^T \end{bmatrix} \cdot \begin{bmatrix} \mathbf{d}(T) \\ \overline{\mathbf{d}}(T) \end{bmatrix} = \begin{bmatrix} \mathbf{F}_f^T \\ \overline{\mathbf{F}}_f^T \end{bmatrix} \quad (32)$$

for the Stokes flow and:

$$\begin{bmatrix} \mathbf{A}^T \end{bmatrix} \cdot \begin{bmatrix} \dot{\mathbf{d}}_c \end{bmatrix} + \begin{bmatrix} \mathbf{K}_c^T \end{bmatrix} \cdot \begin{bmatrix} \mathbf{d}_c \end{bmatrix} = \begin{bmatrix} \mathbf{F}_c^T \end{bmatrix} \quad (33)$$

for the convection-diffusion of solute molecules. For clarity, a quick description and the expression of each submatrix appearing above is provided in “Appendix 3”. We note here that the matrix shown in Eq. (32) is asymmetric and sparse and is solved here using the *LU* factorization method embedded in UMFPACK library of Matlab. A detailed discussion on solution procedure for sparse matrix can be found in reference [55]. The time integration for Eq. (33) is performed with the Backward Euler method, where the errors converge to zeros like $O(\Delta t^2)$ [56].

As discussed earlier, a common issue for X-FEM formulations is that the matrix appears in Eq. (32) might be ill-conditioned [57]. This issue arises when the intersection between the interface and an element occurs near a node; leading to large oscillations in the velocity field and subsequently affecting the rate of convergence. Several methods were developed to address this issue, including the use of modified enrichment functions [58] or the application

of specific preconditioners [59]. In this work, we chose to use the enriched degrees of freedom (EDOF) blocking strategy to remove the EDOF associated with very little support [54]. This method has the advantage that it uses a simple geometrical criterion to determine which EDOF is to be removed.

3.2 Tracking the motion of the interface

As discussed in Sect. 2.1, the normal velocity of the interface is that of the fluid while its tangential velocity is computed in (28). The interface motion can therefore be tracked with the velocity vector $\tilde{\mathbf{v}}$ using the PMIM algorithm [37,38,60]. The procedure follows the following steps:

(a) Interface initialization—We first introduce the initialization procedure at time t_0 followed by the general recursive relations at time t . As shown in Fig. 4a, the interface is discretized with particles whose coordinates $\mathbf{y}$ are chosen as the closest points from each neighboring grid nodes to the interface. Using our knowledge of the initial levelset function $\phi(\mathbf{x}, t_0)$, the vector $\mathbf{y}$ can be expressed as:

$$\mathbf{y} = \mathbf{x} - \phi(\mathbf{x}, t_0) \bar{\mathbf{n}}(\mathbf{x}, t_0) \quad (34)$$

where the normal vector is such that $\bar{\mathbf{n}} = \nabla \phi(\mathbf{x}, t_0)$ and $\mathbf{x}$ is the position vector of a fixed FEM node. To restrict the number of particles on Γ , we define a so-called computational tube of radius λ such as only nodes within this domain ($\phi(\mathbf{x}) < \lambda$) are considered to discretize the interface.

(b) Interface approximation—At an arbitrary time t , an estimation of the local interface geometry (which include the tangential and normal vectors and the mean curvature appearing in 24) is performed by mean of local polynomial approximations. The numerical strategy can be described as follows: for each particle P with coordinate $\mathbf{y}_P$, one can introduce a local orthonormal basis that consists of tangential and normal vectors $\{\bar{\mathbf{a}}_P^t, \bar{\mathbf{n}}_P^t\}$ to the interface (Fig. 4b). These may be derived from the levelset function as follows [61]:

$$\bar{\mathbf{n}}_P^t = \nabla \phi(\mathbf{y}_P, t)$$

$$\bar{\mathbf{a}}_P^t = \bar{\mathbf{n}}_P^t \times \mathbf{m} / |\bar{\mathbf{n}}_P^t \times \mathbf{m}| \quad (35)$$

where $\mathbf{m} = [0 \ 0 \ 1]^T$ is the unit vector normal to the computational domain and $\mathbf{x}$ is the corresponding grid point for the particle. The local geometry of Γ is then evaluated by collecting the closest m particles in the neighborhood of P , with coordinates $\mathbf{y}_1 \dots \mathbf{y}_m$ given, in the local coordinate system, by:

$$\tilde{\mathbf{y}}_i = \begin{Bmatrix} \xi_i^1 \\ \xi_i^2 \end{Bmatrix} = \mathbf{R}^t \cdot (\mathbf{y}_i - \mathbf{y}_p) \quad \text{with} \quad \mathbf{R}^t = \begin{bmatrix} \bar{\mathbf{a}}_p^{t^T} \\ \bar{\mathbf{n}}_p^{t^T} \end{bmatrix} \quad (36)$$

Using the least square fitting method, one can then compute a polynomial:

$$\xi^2(\xi^1) = \sum_{i=0}^n c_i (\xi^1)^i \quad (37)$$

of degree $n < m$ that best fits the particle locations, i.e. the coefficients c_i are determined by minimizing the L^2 difference between the approximation $\xi^2(\xi^1)$ and the nodal values ξ_i^2 . In this way, the local coordinates $\{\xi^1, \xi^2(\xi^1)\}$ form a local parameterization $\mathbf{r}^l(\xi^1, t)$ of the interface around the particle $\mathbf{y}_p$ (Fig. 4b). The corresponding interface global parameterization $\mathbf{r}(\rho, t)$ around the particle $\mathbf{y}_p$ can then be obtained from $\mathbf{r}^l(\xi^1, t)$ as:

$$\mathbf{r}(\rho, t) = (\mathbf{R}^t)^{-1} \mathbf{r}^l(\xi^1, t) + \mathbf{y}_p \quad (38)$$

Furthermore, the tangential and normal vectors $\{\bar{\mathbf{a}}^t, \bar{\mathbf{n}}^t\}$ for an arbitrary point on Γ can now be calculated in the global coordinates as:

$$\bar{\mathbf{a}}^t = \mathbf{r}(\rho, t)_{,\rho} = \mathbf{R}^t \frac{\partial \mathbf{r}^l(\xi^1, t)}{\partial \xi^1}$$

$$\bar{\mathbf{n}}^t = \bar{\mathbf{a}}^t \times \mathbf{m} / |\bar{\mathbf{a}}^t \times \mathbf{m}| \quad (39)$$

(c) Calculation of interface forces—Using the global parameterization of the interface, we are now able to compute the interface force (7) that is determined by the mean curvature. Defining $z'' = z'/\rho^2$, and $z' = z/\rho$, the meridian and azimuthal curvature can then be obtained from $\mathbf{r}(\rho, t)$ as [62]:

$$\kappa_1 = \frac{z''}{(1+z'^2)^{3/2}}, \quad \kappa_2 = \frac{1}{\rho(1+z'^2)^{1/2}} \quad (40)$$

The local mean curvature of the interface $\mathcal{H}$ appearing in (7) is therefore $\mathcal{H} = \frac{1}{2}(\kappa_1 + \kappa_2)$ and (24) is then written as:

$$[p] = \gamma (\kappa_1 + \kappa_2) \quad (41)$$

(d) X-FEM computation of the bulk and interface fields—This step consists of the X-FEM calculation of the unknown variables using (32) and (33) based on the interface geometry determined above.

(e) Interface update—The motion of the interface is captured by updating the particle positions according to the interface velocity $\tilde{\mathbf{v}}^t(\mathbf{y}, t)$ computed by the X-FEM scheme at each timestep. The updated position of each particle is computed by integrating the interface velocity following a second order Runge-Kutta scheme as follows [56]:

$$\begin{aligned} \mathbf{y}^{t+\frac{dt}{2}} &= \mathbf{y}^t + \tilde{\mathbf{v}}(\mathbf{y}^t, t) \frac{dt}{2} + \mathbf{\Omega} \cdot \tilde{\mathbf{v}}(\mathbf{y}^t, t) \frac{dt^2}{4} \\ \mathbf{y}^{t+dt} &= \mathbf{y}^t + \tilde{\mathbf{v}}(\mathbf{y}^{t+\frac{dt}{2}}, t) dt + \mathbf{\Omega} \cdot \tilde{\mathbf{v}}(\mathbf{y}^{t+\frac{dt}{2}}, t) \frac{dt^2}{2} \end{aligned} \quad (42)$$

The time step is chosen according to the Courant- Friedrichs-Lewy (CFL) condition to be $t \sim O(h^2)$ [61]. In Eq. (42), $\mathbf{\Omega}$ is the skew-symmetric spin tensor [37] which, for an axisymmetric problem, reads:

$$\mathbf{\Omega} = \begin{bmatrix} 0 & -\omega_z \\ \omega_z & 0 \end{bmatrix} \quad \text{with} \quad \omega_z = \left(\tilde{v}_{,\xi^2}^{\parallel} - \tilde{v}_{,\xi^1}^{\perp} \right)$$

The levelset function ϕ is then updated and used to identify the new geometry properties. This updated function is expressed by:

$$\phi(\mathbf{y}, t+dt) = g(\mathbf{y}^{t+dt}, \mathbf{x}) \left| \mathbf{y}^{t+dt} - \mathbf{x} \right| \quad (43)$$

where $g(\mathbf{y}^{t+dt}, \mathbf{x})$ is a sign function that determines whether the node $\mathbf{x}$ locates inside or outside the vesicle:

$$g(\mathbf{y}^{t+dt}, \mathbf{x}) = -\text{sgn} \left(\frac{\mathbf{y}^{t+dt} - \mathbf{x}}{|\mathbf{y}^{t+dt} - \mathbf{x}|} \cdot \bar{\mathbf{n}}^t \right)$$

and $\mathbf{y}^{t+dt}$ is the particle corresponding to node $\mathbf{y}$ at time $t + dt$. It is clear that the function g takes a value of -1 inside the vesicle, and 1 outside the vesicle. This step may finally be followed by the interface approximation described in (b) and the algorithm proceeds iteratively until a steady state vesicle motion (constant velocity and deformation) is

observed. The numerical approach is summarized in the general flow chart presented in Fig. 5.

4 Numerical examples

In the following numerical examples, we investigate the phoretic motion of initially spherical vesicles of radius R in a cylindrical channel, of length and radius $2L_y$ and R_c , respectively (Fig. 6). We use an axisymmetric formulation with global coordinates $\{\rho, z\}$ and the ratio of L_y/R_c is set between 0.7 and 0.8. In all examples, governing equations (21–23) are solved using the numerical scheme discussed above with the interface conditions given by (24–26) while the variables (the Peclet number Pe and the surface tension γ^*) are different between examples. Besides, boundary conditions consist of a “no-slip” condition on the wall of the channel and a zero-pressure conditions on the top and bottom boundaries:

$$v_\rho(R_c, z, t) = v_z(R_c, z, t) = 0$$

$$p(\rho, \pm L_y, t) = 0 \quad (44)$$

In addition, “no-flux” conditions are applied for the solute on the channel wall while Dirichlet conditions are imposed on the bottom and top surfaces:

$$\nabla c(R_c, z, t) \cdot \mathbf{n} = 0$$

$$c(\rho, -L_y, t) = c_B$$

$$c(\rho, +L_y, t) = c_T \quad (45)$$

where the bottom and top concentrations c_B and c_T will be defined in each example. Similarly, the initial conditions will be specifically defined for each of the numerical examples.

4.1 Vesicle motion powered by diffusiophoresis

In this example, we study the motion of a spherical vesicle under a solute concentration gradient with the following objectives: (a) validate the model for discontinuous velocity on the interface, (b) investigate the convergence of the proposed scheme by comparing numerical results with well-known analytical solutions and (c) determine the effect of channel boundary on the motion of vesicle. For consistency with existing theoretical work, several assumptions are made: (a) diffusiophoresis is the only contributor to the propulsion of the vesicle, i.e. the presence of solute does not affect the surface energy of the vesicle via the Marangoni effect; (b) the surface tension of the vesicle is high enough so that its

deformation is negligible during motion; (c) the interactions between the interface and solute molecules are small so that the solute concentration c can be varied on the interface due to convection and diffusion (Eq. 10 vanishes).

Analytical solution—Under the above assumptions and using Lamb's general solutions for Stokes flow in spherical geometries [63], Anderson derived the steady state velocity U_a of the vesicle in the infinitely large fluid domain [9]. He found that:

$$U_a = -\frac{3r^-}{2r^+ + 3r^-} \langle v_a \rangle \quad (46)$$

where $r^\pm = \mu^\pm/\mu_w$ are the relative fluid compared with water and $\langle v_a \rangle$ is the average magnitude of the phoretic active flow in the direction of the concentration gradient.

Numerical solution and convergence study—For comparison purposes, we propose to numerically simulate the motion of a spherical vesicle in a long channel with radius $R = R_c/3$. This choice ensures negligible boundary effects on particle motion as the phoretic active flow is known to decay at a rate of ρ^{-3} [9]. To simulate the existence of a concentration gradient $k > 0$, we consider an initial solute distribution that varies along the vertical direction according to $c(\rho, z)_{t=0} = k(z + L_y)$. This is associated with bottom and top conditions $c_B = 0$ and $c_T = 2kL_y$. The interface behavior is then modeled as follows: (a) the surface energy is set $\gamma = 10^6$ so that the vesicle acts as a quasi-rigid particle and (b) we assume a no-slip condition ($\Gamma = 0$) on the inner side of the interface, while an active velocity $\mathbf{v}_a$ is produced on the external side. Further assuming $\Gamma^* = 0$, the conditions in tangential velocity at the interface reads $\mathbf{v}^{\parallel+} - \mathbf{v}_a = \bar{\mathbf{v}}^{\parallel} = \mathbf{v}^{\parallel-}$. Numerically, the domain is discretized spatially with a fixed eulerian mesh with element relative size $h/R = 0.1$ where h is the size of the element and temporally with a timestep that is determined by the CFL condition as $\Delta t = (h/R)^2$ [61].

To assess the performance of the proposed method, we investigated the convergence of error made in calculating the vesicle velocity at a given active flow velocity as a function of both mesh size h and timestep Δt . The L^2 -error e_v^2 in vesicle velocity is calculated as:

$$e_v^2 = \left[\left(\frac{U_a}{\langle v_s \rangle} - \frac{U_n}{\langle v_s \rangle} \right)^2 \right]^{1/2} \quad (47)$$

where U_a is obtained from Eq. (46) and U_n is obtained numerically by computing the velocity of the vesicle's center of mass at each timestep. The convergence study with respect to the mesh size is carried out for two different vesicle size: $R = R_c/2$ and $R = R_c/3$. Results presented in Fig. 7a show a rate of convergence $O(h^{2.1})$ that agrees well results obtained for the grid-based particle method showing convergence rates around $O(h^2)$ [61]. A convergence study with respect to timestep was performed in a similar way by fixing the mesh size as $h/R = 0.1$ (Fig. 7b). We report here a linear trends in the log-log plot with rates of convergence

for both vesicle sizes around $\mathcal{O}(h^{1.9})$. This result is expected for a second-ordered Runge–Kutta time integration scheme. [56].

From a physical perspective, the model give a number of insights on vesicle motion. For instance, we show in Fig. 8a the dependency of the vesicle U_n on the viscosity of the external fluid in and out the vesicle domain. One clearly sees, in agreement with the analytical prediction, that the velocity of stiffer vesicles (high r^-) is larger than their soft, fluid-like counterparts (low r^-). This result can be explained by the fact that soft vesicles exhibit significant circulation within their body (Fig. 8c) that tends to dissipates energy and slow them down. Moreover, we show in Fig. 8b the nonequilibrium behavior of the vesicle as it transitions between its rest state and its steady state (moving at constant velocity). We see that the vesicle starts moving at a velocity that is much larger than it steady state velocity and that this velocity decreases exponentially to asymptotically reach its equilibrium value U_n . One finds that this trends is explained by the redistribution of solute molecules around the vesicle during motion. It can indeed be seen in the inset of Fig. 8b that the local concentration gradient gradually decreases due to convection and diffusion in the vicinity of the interface Γ , which effectively decrease the driving force for vesicle motion.

Boundary effect—Despite the good consistency between analytical and numerical results, one clearly observe minor differences in the numerical results for different vesicle size. Such differences are explained by the boundary effect of the channel wall. Generally, the existence of this boundary has two effects on the vesicle speed: first, the solute concentration on the vesicle surface can be altered, which will either enhance or decrease its velocity; second, the wall locally affects the fluid velocity which will alter the vesicle velocity as well [64]. In general, the boundary effect on the diffusiophoresis problem is quite complicated and can be affected by many factors. In our study, we investigate the strength of boundary effect by finding the relationship between the steady vesicle velocity U_n and the relative vesicle shape R/R_c . The relative vesicle size R/R_c is varied between 0.25 and 0.9 with a mesh size $h/R = 0.1$ and timestep $\tau = (h/R)^2$. Figure 9 shows the steady vesicle velocity with different relative sizes, where one could see that there exists a critical relative size $R/R_c \approx 0.5$, above which the steady velocity drops sharply. When the vesicle relative size is smaller than 0.5, however, the steady velocity is independent of the vesicle size.

Diffusiophoresis of a soft droplet—When the vesicle surface is soft (low surface tension), its shape will change and affect its traveling velocity [20]. This issue is however difficult to address with analytical methods due to the complexity fluid-interface interaction problem. We therefore use the presented numerical strategy to study and predict the equilibrium shape of the vesicles with various interface stiffness, and further compare their steady shape and velocity with rigid particles obtained previously. In this example, the relative stiffness of the vesicle interface can be described by a nondimensional parameter $\beta = \gamma / \mu M \nabla_m c$ where $\nabla_m c$ is the average magnitude of the initial concentration gradient, μ the fluid viscosity and M the surface mobility coefficient given by (12). In this way, the effective stiffness of the vesicle is proportional to the value of β . To characterize the shape of the vesicle, we then introduce another nondimensional parameter in the form $\mathcal{H}^* = \mathcal{H}_{\min} / \mathcal{H}_{\max}$ where $\mathcal{H}_{\min}$ and $\mathcal{H}_{\max}$ are the minima and maxima of local mean curvature of the vesicle at

steady state, respectively. With this definition, $\mathcal{H}^*=1$ corresponds to a spherical vesicle while $\mathcal{H}^* \leq 1$ represents a deformed shape as shown in Fig. 10c.

To better understand the role of surface tension on vesicle deformation during diffusiophoresis, we first investigated in Fig. 10a how the vesicle shape parameter $\mathcal{H}^*$ was affected by β at constant concentration gradient. As expected, we observe that softer vesicles (small β) became slightly pear-like in shape while stiffer vesicles (large β) did not undergo significant deformations and remained spherical (Fig. 10c). The effect of deformability on speed was then examined by plotting the normalized vesicle velocity $U^* = U_r/U_0$ (U_0 being the velocity of a rigid particle) against the shape parameter $\mathcal{H}^*$. Results shown in Fig. 10b clearly indicate that a non-deformable, spherical vesicle tends to exhibit a larger velocity than a softer counterpart. This trend can be explained by the difference in solute concentration profile shown in Fig. 10c: the deformation of soft droplet has significant disturbance on the solute concentration in its neighborhood, which tends to lower the local concentration gradient. By contrast, stiffer vesicles see a fairly uniform concentration gradient near their surface, a condition that seems optimal to achieve greater velocities.

4.2 Vesicle motion powered by the Marangoni effect

In the second numerical example, we investigate the motion of a vesicle powered by the Marangoni effect. We particularly focus on the problem of a vesicle subjected to the competing effects of a temperature gradient and a gravitational field. For this, we consider a vesicle in a vertical tube as shown in Fig. 11a whose mass density is larger than the surrounding fluid. For this problem, the Stokes flow equation becomes:

$$\mu \nabla^2 \mathbf{v} - \nabla p - \rho \mathbf{g} = 0 \quad (48)$$

where ρ is the mass density of the fluid and $\mathbf{g}$ the gravitational acceleration. Although in these conditions, the vesicle is expected to sink, the presence of a temperature gradient in the vertical direction may create a competing force due to the Marangoni effect. For a specific temperature gradient, we aim here to determine the vesicle size for the buoyancy and Marangoni forces to neutralize so that the vesicle remains motionless in the tube.

Analytical solution—This problem was theoretically addressed by Young's et al. [5] in an infinite domain subjected to a temperature gradient. In Young's study, the following assumptions were made: (a) The convection effect in steady state is negligible; this implies that the temperature field verifies the Laplace equation $\nabla^2 c = 0$. (b) The vesicle is nondeformable and spherical. (c) On the interface, the phoretic active flow $\mathbf{v}_a$ vanishes and “no-slip” conditions are applied on the interface ($\ell = \ell' = 0$), i.e. we have $\mathbf{v}|_+ = \mathbf{v}|_-$. Under those assumptions, the critical vesicle radius to keep the vesicle motionless is:

$$R_s = \frac{3\gamma'}{2g(\rho^- - \rho^+)} \frac{dc}{dz} \quad (49)$$

where ρ^- and ρ^+ are the fluid density inside and outside the vesicle, respectively, while $\gamma' = d\gamma/dc$ is the temperature coefficient of surface tension. Young et al. [5] experimentally measured this coefficient for three silicone oils and found $\gamma'_A = -0.06 \text{ dyne} \cdot \text{cm}^{-1} \text{C}^{-1}$; $\gamma'_B = -0.07 \text{ dyne} \cdot \text{cm}^{-1} \text{C}^{-1}$ and $\gamma'_C = -0.08 \text{ dyne} \cdot \text{cm}^{-1} \text{C}^{-1}$, respectively.

Numerical study—Boundary conditions corresponding to this problem are as follows: the temperature at the top and bottom edge of the domain are $c_T = 360 \text{ K}$ and $c_B = 300 \text{ K}$, respectively. A vertical temperature gradient is then naturally formed at steady state (Fig. 11a). Assuming the interface has the same thermal-conductivity as the solution, the energy conservation Eq. (19) is automatically satisfied on the interface by the laplacian equation $\nabla^2 c = 0$, where temperature is continuous across the interface. We further assume a linear relation between surface tension and temperature in the form:

$$\gamma = \gamma_0 + \gamma' (c - c_0) \quad (50)$$

where γ_0 is the surface energy at reference temperature c_0 and γ' is the surface thermal coefficient. To provide comparisons with experimental results, we use the surface tension of water $\gamma_0 = 0.072 \text{ N/m}$ at room temperature $c_0 = 300 \text{ K}$, an external fluid density $\rho^+ = 1000 \text{ kg/m}^3$ corresponding to water and an internal fluid density of $\rho^- = 1250 \text{ kg/m}^3$. Based on the convergence study shown in Fig. 7, the fluid domain is discretized by the mesh size of $h/R = 0.1$ and the timestep is set as $\Delta t = (h/R)^2$ to achieve computationally efficiency without losing accuracy. To avoid boundary effects, we considered a ratio between the vesicle and channel radii of $R/R_c = 1/3$.

Results—Numerically, the critical vesicle radius R_s was estimated (for a given temperature gradient dc/dz) by spanning a range of radii and identifying the particular value at which the vesicle remained motionless. To verify our approach, we first performed a comparison between numerical prediction of R_s and the analytical solution for three values of the coefficient γ' . Figure 11c shows that a very good agreement is obtained for all three thermal coefficients and a range of temperature gradients. One can see that, as expected, the critical vesicle size (hence its weight) must increase with temperature gradient to counteract the Marangoni effect. The observed linear trend is not surprising since the weight of a vesicle is related to its volume, on the order of R^3 , while the Marangoni effect is related to its surface area on the order of R^2 . The relationship between gravitational force and the Marangoni force must therefore be on the order of R . Similarly, as the strength of the Marangoni increases, as described with a higher thermal coefficient γ' , one observed a linear rise in critical vesicle size. As shown in Fig. 11c we have also compared the model prediction of the resultant temperature profile and fluid velocity of fluid at steady state. The presented results agree with the analytical solution of Young et al. [5], which clearly show the existence of a local pressure gradient around the vesicle as a result of the variation in surface tension. This feature is responsible for a strong fluid circulation inside the vesicle.

4.3 Spontaneous motion of a vesicle in solution

For the third numerical example, we investigate the complex problem of the spontaneous motion of a rigid particle by diffusiophoresis in an initially isotropic solute concentration. For this, consider a static vesicle immersed in a solution of radially distributed solute particle shown in Fig. 12a. It has been shown in [12] that a stable dynamic state may however be obtained by breaking the symmetry of the problem through the application of a small perturbation to the particle velocity. The mechanics of this phenomenon relies on the competition between the convection and the surface adsorption of solute molecules; on the one hand, convection tends to re-distributing the solute molecules in the fluid domain and break the azimuthal isotropy while on the other hand, surface adsorption maintains the azimuthal isotropy and the concentration gradient in the radial direction.

Analytical solution

To develop an analytical solution, Michelin et al. [12] considered a rigid spherical particle immersed in a infinitely large fluid domain in which the initial solute concentration was expressed as (first inset in Fig. 12a):

$$c(r, \theta, 0) = c_0(R, \theta, 0) - kr \quad (51)$$

where r is the distance to the center of the particle, $c_0(R, \theta, 0)$ the initial concentration on the particle surface and k the concentration gradient in the radial direction. Using the reciprocal theorem and decomposing the phoretic active flow $\mathbf{v}_a$ along the so called “squirming mode”, Michelin et al. [12,65] found that there exists a size-dependent critical Peclet number Pe above which a dynamic state is achieved. For small Peclet numbers ($Pe \ll 4$), the active particle velocity decreases after the perturbation is applied and no net motion is achieved in the long term. For higher Peclet numbers however ($Pe > 4$), the velocity increases and the front-back asymmetry is amplified until a dynamic steady state is achieved. Moreover, we found that to achieve a dynamic steady state in the long term, the surface mobility M and the normal diffusion rate from the outer edge $(-\bar{\mathbf{n}} \cdot D\nabla c)^+$ must satisfy $M(-\bar{\mathbf{n}} \cdot D\nabla c)^+ = 1$. In other words, solute molecules must be consumed or generated by the interface during the autophoresis.

Numerical solution—A numerical solution was obtained based on the boundary conditions shown in Eq. (44) and $L_y/R_c = 0.7$ and $R/R_c = 0.45$. According to Fig. 9, these dimensions ensure negligible boundary effects. Initial and boundary conditions for the solute concentration are given by Eqs. (51) and (45) with $c_B = c_T = 0$, respectively. For consistency with the analytical work, the following model parameters are chosen: (a) the parameter r^* in Eq. (21) is set as $r^* = 10^6$ so that the fluid inside the particle is highly viscous, (b) The surface tension is taken to be $\gamma = 10^6$ so that the vesicle behaves like a near rigid particle. (c) The slip lengths are $\ell^* = \ell^* = 0$. In other words, $\mathbf{v}_a^{\parallel-} = \bar{\mathbf{v}}^{\parallel}$ and $\mathbf{v}_a^{\parallel+} = \bar{\mathbf{v}}^{\parallel} = \mathbf{v}_a$ and (d) The magnitude of normal solute flux $(-\bar{\mathbf{n}} \cdot D\nabla c)^+$ is modified in (10) and (11) to satisfy $M(-\bar{\mathbf{n}} \cdot D\nabla c)^+ = 1$ for steady velocity. Finally, similar to the previous example, the

computational domain was discretized with a regular FEM mesh of element size $h/R = 0.1$ and timestep $\Delta t = (h/R)^2$.

Results—We first used the numerical model to predict the vesicle's steady velocity U^∞ as a function of the Peclet number in Eq. (23). We show in Fig. 12a comparison of the numerical prediction (dots) and the analytical solution (solid line) found in [12]. We note an excellent agreement between the two approaches with a predicted critical Peclet number $Pe = 4$ below which no steady state motion is observed and the existence of an optimum Peclet number $Pe \approx 9$ at which the steady velocity is maximized. The solute concentration are also plotted in the insets of Fig. 12b for three Peclet numbers ($Pe = 1, 5$ and 15). It becomes clear here that the front-back asymmetry increases with the Peclet number; this in turns allows greater velocities. We next investigated the ability of the mode in predicting the non-equilibrium vesicle response after the initial perturbation was applied. In this context, Fig. 12b display both numerical and analytical results for the time evolution of the vesicle velocity at $Pe = 6$ from its initial to its steady state. We again observe a good agreement between the methods and their ability to capture the sharp increase in velocity immediately after being subjected to the perturbation. We also observe the presence of a peak velocity value, after which the vesicle asymptotically reaches its steady state speed. Finally, our numerical results exhibit a strong correlation between the front-back asymmetry in solute distribution during the process and the vesicle velocity (insets of Fig. 12b).

5 Conclusion

In summary, we introduced a numerical strategy that combines XFEM and the PMIM method to model the self-propulsion of a surface-active vesicle in concentration gradients. We showed that this approach can naturally accounts for various field discontinuities across the vesicle interface encountered in both diffusiophoresis and Marangoni-driven vesicles (XFEM) and provides an efficient way of describing the motion and shape changes of the vesicle interface (PMIM). Through the presentation of three example problems, we showed that the method was efficient and accurate in describing vesicle motion in various conditions and reproduced a number of known analytical results. The presented numerical approach could also help understand some complex phenomena that could not be addressed with analytical approaches, such as the effect of vesicle deformation during diffusiophoresis and be well in conjunction with self-learning algorithms [66] to better characterize the system. This work therefore constitutes an important stepping stone for future studies that aim to understand the physics of complex systems such as multiple vesicle interactions, vesicle propulsion through porous media [67,68], flow cell electrophoresis [69] or the chemical targeting of cells and vesicles in biological systems [70]. The computational design of such biomaterials is indeed the key to the future of targeted, and personalized medicine [71,72].

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Appendix 1: Expressions and derivatives of shape functions

In the numerical study, XFEM is implemented in the element shape functions to account for the discontinuities. For split elements, the extended interpolation matrices $\mathbf{N}^4(x)$ and $\mathbf{N}^9(x)$ in Eq. (35) and (36) have the form:

$$\mathbf{N}^4(x) = \begin{bmatrix} N_1^4 & \dots & N_4^4 \Psi_1 N_1^4 & \dots & \Psi_4 N_4^4 \end{bmatrix}$$

$$\mathbf{N}^9(\mathbf{x}) = \begin{bmatrix} N_1^9 & 0 & \dots & N_9^9 & 0 & \Psi_1 N_1^9 & 0 & \dots & \Psi_9 N_9^9 & 0 \\ 0 & N_1^9 & 0 & \dots & N_9^9 & 0 & \Psi_1 N_1^9 & 0 & \dots & \Psi_9 N_9^9 \end{bmatrix} \quad (52)$$

where $\Psi_I = H - H_I$ is the Heaviside enrichment function applying on the I th node. For normal elements that are not splitted, the Heaviside enrichment functions vanish to zero and only the normal shape functions are retain. On the interface, a simple $1 - D$ shape function is used to interpolate the quantities on the interface:

$$\bar{\mathbf{N}} = \begin{bmatrix} \bar{N}_1 & \bar{N}_2 \end{bmatrix} \quad (53)$$

To compute the deformation rate of the fluid, the rate of deformation of fluid and the divergence of fluid are written as:

$$\mathbf{D} = (\nabla \mathbf{v})^s = \mathbf{B} \cdot \mathbf{v}^e \quad \text{and} \quad \nabla \cdot \mathbf{v} = \hat{\mathbf{B}} \cdot \mathbf{v}^e$$

we write the rate $\mathbf{B}$ and $\hat{\mathbf{B}}$ matrices that are related to the nodal velocities to deformation rate and velocity divergence in the cylindrical coordinates as

$$\mathbf{B} = [\mathbf{B}_1 \dots \mathbf{B}_{n9+m9}], \quad \hat{\mathbf{B}} = [\hat{\mathbf{B}}_1 \dots \hat{\mathbf{B}}_{n9+m9}]$$

with

$$\mathbf{B}_I = \begin{bmatrix} \frac{\partial N_I^9(\mathbf{x})}{\partial \rho} & 0 \\ 0 & \frac{\partial N_I^9(\mathbf{x})}{\partial z} \\ \frac{N_I^9(\mathbf{x})}{r} & \frac{\partial N_I^9(\mathbf{x})}{\partial \rho} \\ \frac{\partial N_I^9(\mathbf{x})}{\partial z} & \frac{\partial N_I^9(\mathbf{x})}{\partial \rho} \end{bmatrix}, \quad (54)$$

$$\hat{\mathbf{B}}_I = \begin{bmatrix} \frac{\partial N_I^9(\mathbf{x})}{\partial \rho} + \frac{N_I^9(\mathbf{x})}{r} \frac{\partial N_I^9(\mathbf{x})}{\partial z} \end{bmatrix}$$

where the subscript n corresponds to the normal element nodes and m is corresponded to the enriched degrees of freedom. Similarly, the matrix that relates to the spatial rate of change in concentration reads:

$$\mathbf{B}^4 = [\mathbf{B}_1^4 \dots \mathbf{B}_{n4+m4}^4]$$

with

$$\mathbf{B}_I^4 = \left[\frac{\partial N_I^4(\mathbf{x})}{\partial \rho} \frac{\partial N_I^9(\mathbf{x})}{\partial z} \right]^T, \quad (55)$$

Appendix 2: Discretized weak form

With the matrix forms of the fields given, plug in the matrix form for $\mathbf{v}$, p in Eq. (30) and c in Eq. (31), the discretized weak form for fluid is then read:

$$\begin{aligned} & \sum_{e=1}^{nel} \{\omega_v^{eT}\} \left[\int_{\Omega^e} (r \mathbf{B}^T \cdot \mathbf{B} \cdot \mathbf{v}^e - \mathbf{B}^T \cdot \mathbf{N}^4 \cdot \mathbf{p}^e) r d\Omega^e + \int_{\Gamma^e} \left(\mathbf{N}^{9T} \cdot \mathbf{a}^T \cdot \frac{r^+}{l^+} \bar{\mathbf{N}} \cdot \lambda^{e+} r d\Gamma^e \right. \right. \\ & \quad \left. \left. - \int_{\Gamma^e} \mathbf{N}^{9T} \cdot \mathbf{a}^T \cdot \frac{r^-}{l^-} \bar{\mathbf{N}} \lambda^{e-} \right) r d\Gamma^e \right. \\ & \quad \left. + \int_{\Gamma^e} \mathbf{N}^{9T} \cdot \bar{\mathbf{f}} r d\Gamma^e \right] \\ & + \sum_{e=1}^{nel} \{\omega_p\}^T \left[\int_{\Omega^e} \mathbf{N}^{4T} \cdot \hat{\mathbf{B}} \cdot \mathbf{v}^e r d\Omega^e + \int_{\Gamma^e} \mathbf{N}_{\square}^{4T} \cdot \bar{\mathbf{N}} \cdot \lambda^p r d\Gamma^e + \sum_{e=1}^{nel} \{\omega_{\lambda_p}\}^T \left[\int_{\Gamma^e} \bar{\mathbf{N}}^T \cdot \mathbf{N}_{\square}^4 \cdot \mathbf{p}^e r d\Gamma^e - \int_{\Gamma^e} \bar{\mathbf{N}}^T \cdot \bar{\mathbf{f}} r d\Gamma^e \right] + \sum_{e=1}^{nel} \{\omega_{\lambda}\}^e \right. \\ & + \sum_{e=1}^{nel} \{\omega_{\lambda-}\}^T \left[\int_{\Gamma^e} \bar{\mathbf{N}}^T \cdot \left(r \mathbf{a}^T \cdot \mathbf{P}^\perp \cdot \mathbf{B}_- - \frac{r^-}{l^-} \mathbf{a} \cdot \mathbf{N}_v \right) \cdot \mathbf{v}^e r d\Gamma^e + \int_{\Gamma^e} \bar{\mathbf{N}}^T \cdot \frac{r^-}{l^-} \bar{\mathbf{N}} \cdot \bar{\mathbf{v}}^{\parallel e} r d\Gamma^e \right] + \sum_{e=1}^{nel} \{\omega_{\bar{\mathbf{v}}^{\parallel}}\}^T \left[\int_{\Gamma^e} \bar{\mathbf{N}} \cdot \left(-\frac{r^+}{l^+} \mathbf{a} \cdot \mathbf{N} \right. \right. \\ & + \int_{\Gamma^e} \bar{\mathbf{N}} \cdot \left(-\frac{r^-}{l^-} \bar{\mathbf{N}} \cdot \lambda^- \right) r d\Gamma^e \\ & \quad \left. \left. + \int_{\Gamma^e} \bar{\mathbf{N}}^T \cdot \left(\frac{r^+}{l^+} - \frac{r^-}{l^-} \right) \bar{\mathbf{N}} \cdot \bar{\mathbf{v}}^{\parallel} r d\Gamma^e - \int_{\Gamma^e} \bar{\mathbf{N}}^T \cdot \left(\frac{r^+}{l^+} \mathbf{v}_a \right) r d\Gamma^e \right] = 0 \right. \\ & \quad \left. (56) \right] \end{aligned}$$

where the $+$ and $-$ sign on the $\mathbf{N}$ and $\mathbf{B}$ are associated with the interpolation on the $+$ or $-$ side of the interface respectively. The matrix $\mathbf{N}_{\square}^4 = [0 \dots 0 \ N_1^4 \dots N_4^4]$ is associated with the pressure jump at the interface.

In a similar way, the discretized weak form for transportation of solute reads:

$$\begin{aligned}
& \sum_{e=1}^{nel} \{\omega_c\}^T \left[\int_{\Omega^e} \mathbf{N}^{4T} \cdot \mathbf{N}^4 \cdot \dot{\mathbf{c}}^e r d\Omega^e + \int_{\Omega^e} \mathbf{N}^{4T} \cdot \mathbf{v}^{eT} \cdot \mathbf{B}^4 \cdot \mathbf{c}^e r d\Omega^e \right. \\
& \quad + \int_{\Omega^e} \mathbf{B}^{4T} \cdot \mathbf{B}^4 \cdot \mathbf{c}^e r d\Gamma^e \\
& \quad + \int_{\Gamma^e} \overline{\mathbf{N}}^T \cdot \mathbf{N}_{\square}^4 \cdot \mathbf{c}^e r d\Gamma^e \\
& \quad - \int_{\Gamma^e} \overline{\mathbf{N}}^T \cdot [\\
& \quad - \mathbf{n} \cdot \mathbf{B}^4 \cdot \mathbf{c}_t \\
& \quad + \frac{1}{K} (\mathbf{N}^+ - \mathbf{N}^-) \cdot \mathbf{c}_t \\
& \quad \left. + K \mathbf{P}^{\parallel} \cdot \mathbf{B}^4 \cdot \mathbf{q}^{\parallel} r d\Gamma^e + \int_{\Gamma^e} \overline{\mathbf{N}}^T \cdot \left[-\mathbf{n} \cdot \mathbf{B}^4 \cdot \mathbf{c}_t + \frac{1}{K} (\mathbf{N}^+ - \mathbf{N}^-) \cdot \mathbf{c}_t + K \mathbf{P}^{\parallel} \cdot \mathbf{B}^4 \cdot \mathbf{q}^{\parallel} r d\Gamma^e \right] \right. \\
& \quad + \sum_{e=1}^{nel} \{\omega_{\lambda c}\}^T \left[\int_{\Gamma^e} \overline{\mathbf{N}}^T \cdot \mathbf{N}_{\square}^4 \cdot \mathbf{c}^e r d\Gamma^e \right. \\
& \quad \left. + \int_{\Gamma^e} \overline{\mathbf{N}}^T \cdot \left[-\mathbf{n} \cdot \mathbf{B}^4 \cdot \mathbf{c}_t + \frac{1}{K} (\mathbf{N}^+ - \mathbf{N}^-) \cdot \mathbf{c}_t + K \mathbf{P}^{\parallel} \cdot \mathbf{B}^4 \cdot \mathbf{q}^{\parallel} r d\Gamma^e \right] \right] = 0
\end{aligned}$$

where $\mathbf{v}^e$ is the calculated fluid velocity from the stokes equation, $\mathbf{c}_t$ is the nodal value of solute concentration obtained from previous timestep, $\dot{\mathbf{c}}^e$ is the rate of change of solute concentration. The tangential flux $\mathbf{q}^{\parallel}$ is computed according to Eq. (11) for solute concentration or (18) for temperature using the calculated nodal value $\mathbf{c}_t$.

Appendix 3: Matrix form

For Stokes flow problem (Eq. 33), in each element, the vector $\mathbf{d}(t)$ is composed of the fluid degrees of freedom $\mathbf{d}(t) = \mathbf{v}(t), \mathbf{p}(t)^T$ and $\overline{\mathbf{d}}(t)$ is composed of the interface degrees of freedom $\overline{\mathbf{d}}(t) = [\overline{v}^{\parallel}, \lambda_p, \lambda^+, \lambda^-]^T$. The submatrix $\mathbf{K}^T$ and $\overline{\mathbf{K}}^T$ are corresponding to fluid domain Ω and interface Γ respectively, while $\mathbf{I}_1^t$ and $\mathbf{I}_1^T$ are associated to fluid-interface interactions. The global force vector $\mathbf{F}_f^t$ is corresponding to the external force as well as the force produced by the interface, and $\overline{\mathbf{F}}_f^T$ is associated with the jump conditions on the interface including pressure and tangential velocity. The detailed expressions of for the submatrices in (33) are:

$$\mathbf{K}_e^t = \begin{bmatrix} \mathbf{K}_{vv}^e & \mathbf{K}_{vp}^e \\ \mathbf{K}_{pv}^e & 0 \end{bmatrix} \quad \overline{\mathbf{K}}_e^t = \begin{bmatrix} \mathbf{K}_{\overline{v}^{\parallel}\overline{v}^{\parallel}}^e & 0 & \mathbf{K}_{\overline{v}^{\parallel}\lambda^+}^e & \mathbf{K}_{\overline{v}^{\parallel}\lambda^-}^e \\ 0 & 0 & 0 & 0 \\ \mathbf{K}_{\lambda^+\overline{v}^{\parallel}}^e & 0 & 0 & 0 \\ \mathbf{K}_{\lambda^-\overline{v}^{\parallel}}^e & 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{I}_{e1}^t = \begin{bmatrix} \mathbf{K}_{\bar{v}\parallel v}^e & 0 \\ 0 & \mathbf{K}_{\lambda_p p}^e \\ \mathbf{K}_{\lambda^+ v}^e & 0 \\ \mathbf{K}_{\lambda^- v}^e & 0 \end{bmatrix} \quad \mathbf{I}_{e2}^t = \begin{bmatrix} 0 & 0 & \mathbf{K}_{v\lambda^+}^e & \mathbf{K}_{v\lambda^-}^e \\ 0 & \mathbf{K}_{p\lambda_p}^e & 0 & 0 \end{bmatrix}$$

$$\mathbf{F}_{fe}^t = \begin{bmatrix} \mathbf{F}_v^e & \mathbf{F}_p^e \end{bmatrix}^T \quad \bar{\mathbf{F}}_{fe}^t = \begin{bmatrix} \mathbf{F}_{\bar{v}\parallel}^e & \mathbf{F}_{\lambda_p}^e & \mathbf{F}_{\lambda^+}^e & 0 \end{bmatrix}^T$$

with the element matrices forms:

$$\mathbf{K}_{vv}^e = \int_{\Omega^e} r \mathbf{B}^T \cdot \mathbf{B} \, r d\Omega^e$$

$$\mathbf{K}_{vp}^e = \int_{\Omega^e} -\mathbf{B}^T \cdot \mathbf{N}^4 \, r d\Omega^e$$

$$\mathbf{K}_{v\lambda^+}^e = \int_{\Gamma^e} \mathbf{N}_+^T \cdot \mathbf{a} \frac{r^+}{l^+} \bar{\mathbf{N}} \, r d\Gamma^e$$

$$\mathbf{K}_{v\lambda^-}^e = \int_{\Gamma^e} -\mathbf{N}_+^T \cdot \mathbf{a} \frac{r^-}{l^-} \bar{\mathbf{N}} \, r d\Gamma^e$$

$$\mathbf{K}_{pv}^e = \int_{\Omega^e} -\mathbf{N}^{4T} \cdot \mathbf{B} \, r d\Omega^e$$

$$\mathbf{K}_{p\lambda_p}^e = \int_{\Gamma^e} \mathbf{N}_{[]}^{4T} \cdot \bar{\mathbf{N}} \, r d\Gamma^e$$

$$\mathbf{K}_{\bar{v}\parallel v}^e = \int_{\Gamma^e} \bar{\mathbf{N}}^T \cdot \left(-\frac{r}{l^+} \mathbf{a} \cdot \mathbf{N}_+^9 - \frac{r}{l^-} \mathbf{a} \cdot \mathbf{N}_-^9 \right) r d\Gamma^e$$

$$\mathbf{K}_{\bar{v}\parallel \bar{v}\parallel}^e = \int_{\Gamma^e} \bar{\mathbf{N}}^T \left(\frac{r^+}{l^+} + \frac{r^-}{l^-} \right) \bar{\mathbf{N}} \, r d\Gamma^e$$

$$\mathbf{K}_{\bar{v}\parallel \lambda^+}^e = \int_{\Gamma^e} \bar{\mathbf{N}}^T \cdot \frac{r^+}{l^+} \bar{\mathbf{N}} \, r d\Gamma^e$$

$$\mathbf{K}_{\bar{v}||\lambda^-} = \int_{\Gamma^e} \bar{\mathbf{N}}^T \cdot \frac{r^-}{l^-} \bar{\mathbf{N}} r d\Gamma^e$$

$$\mathbf{K}_{\lambda_p P} = \int_{\Gamma^e} -\bar{\mathbf{N}}^T \cdot \mathbf{N}_{\square}^4 r d\Gamma^e$$

$$\mathbf{K}_{\lambda^+ v} = \int_{\Gamma^e} \bar{\mathbf{N}}^T \cdot \left(r^+ \mathbf{a}^T \cdot \mathbf{P}^\perp \cdot \mathbf{B}_+ + \frac{r^+}{l^+} \mathbf{N}_+ \cdot \mathbf{a} \right) r d\Gamma^e$$

$$\mathbf{K}_{\lambda^+ \bar{v}||} = \int_{\Gamma^e} \bar{\mathbf{N}}^T \cdot \frac{r^+}{l^+} \bar{\mathbf{N}} r d\Gamma^e$$

$$\mathbf{K}_{\lambda^- v} = \int_{\Gamma^e} \bar{\mathbf{N}}^T \cdot \left(r^- \mathbf{a}^T \cdot \mathbf{P}^\perp \cdot \mathbf{B}_- - \frac{r^-}{l^-} \mathbf{N}_- \cdot \mathbf{a} \right) r d\Gamma^e$$

$$\mathbf{K}_{\lambda^- \bar{v}||} = \int_{\Gamma^e} \bar{\mathbf{N}}^T \cdot \frac{r^-}{l^-} \bar{\mathbf{N}} r d\Gamma^e$$

with the element force vector:

$$\mathbf{F}_v^e = \int_{\Omega^e} -\mathbf{N}^T \cdot \bar{\mathbf{f}} r d\Omega^e$$

$$\mathbf{F}_{\bar{v}||}^e = \int_{\Gamma^e} \bar{\mathbf{N}}^T \cdot \left(\frac{r}{l^+} \mathbf{v}_a \right) r d\Gamma^e$$

$$\mathbf{F}_{\lambda_p}^e = \int_{\Gamma^e} \bar{\mathbf{N}}^T \cdot \bar{\mathbf{f}} r d\Gamma^e$$

$$\mathbf{F}_{\lambda^+}^e = \int_{\Gamma^e} -\bar{\mathbf{N}}^T \cdot \frac{r}{l^+} \mathbf{v}_a r d\Gamma^e$$

Regarding the transport problem (34), the vector $[\dot{\mathbf{d}}_c] = [\dot{c}, 0]^T$ is composed of the rate of change of the solute concentration and the submatrix $\mathbf{A}^T$ is corresponding to the fluid domain. The vector $[\mathbf{d}_c] = [\mathbf{c}, \lambda_c]^T$, is composed of the solute concentration degrees of freedom, with the submatrix $\mathbf{K}_c$ is associated with the convection and diffusion of solute

molecules. The global force vector $\mathbf{F}_c$ accounts for the jump of concentration on the interface, as well as the emission or adsorption of solute on the interface. The detailed expressions of submatrices for Eq. (34) are:

$$\mathbf{A}_e^t = \begin{bmatrix} \mathbf{K}_{cc}^e & 0 \\ 0 & 0 \end{bmatrix} \quad \mathbf{K}_{c_e}^t = \begin{bmatrix} \mathbf{K}_{cv}^e & \mathbf{K}_{c\lambda}^e \\ \mathbf{K}_{\lambda c}^e & 0 \end{bmatrix}$$

$$\mathbf{F}_c^e = [\mathbf{F}_c \mathbf{F}_{\lambda c}] \quad (57)$$

and the element matrices written as:

$$\mathbf{K}_{cc}^e = \int_{\Omega^e} \mathbf{N}^{4T} \cdot \mathbf{N}^4 r d\Omega^e$$

$$\mathbf{K}_{cv}^e = \int_{\Omega^e} (\mathbf{N}^{4T} \cdot \mathbf{N} \cdot \mathbf{v}_s^T \cdot \mathbf{B}^4 + \mathbf{B}^{4T} \cdot \mathbf{B}^4) r d\Omega^e$$

$$\mathbf{K}_{c\lambda}^e = \int_{\Gamma^e} \bar{\mathbf{N}}^T \cdot \mathbf{N}_{[]}^4 r d\Gamma^e$$

$$\mathbf{K}_{\lambda c}^e = \int_{\Gamma^e} \mathbf{N}_{[]}^4 \cdot \bar{\mathbf{N}} r d\Gamma^e$$

with the force vector:

$$\mathbf{F}_c^e = \int_{\Gamma^e} -\bar{\mathbf{N}}^T \cdot [-\mathbf{n}^T \cdot \mathbf{B}^4 \cdot \mathbf{c}_t + \frac{1}{K} (\mathbf{N}_+^4 - \mathbf{N}_-^4) \cdot \mathbf{c}_t + K \mathbf{P}^{\parallel} \cdot \mathbf{B}^4 \cdot \mathbf{q}^{\parallel}] r d\Gamma^e.$$

$$\mathbf{F}_{\lambda c}^e = \int_{\Gamma^e} \bar{\mathbf{N}}^T \cdot [-\mathbf{n}^T \cdot \mathbf{B}^4 \cdot \mathbf{c}_t + \frac{1}{K} (\mathbf{N}_+^4 - \mathbf{N}_-^4) \cdot \mathbf{c}_t + K \mathbf{P}^{\parallel} \cdot \mathbf{B}^4 \cdot \mathbf{q}^{\parallel}] r d\Gamma^e.$$

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Fig. 1.

Phoretic motion of a vesicle in the solution due to the variation in solute concentration or temperature. The vesicle moves from the lower concentration/temperature edge to the higher edge and triggers the flow of neighboring fluid. The domain is divided into three parts, the fluid domain inside the vesicle Ω^- and outside the vesicle Ω^+ , as well as the vesicle interface Γ

Fig. 2.

a Diffusiophoresis: active flow $\mathbf{v}_a$ generated from solute concentration gradient; **b** Marangoni effect: variation in surface tension of interface due to temperature gradient. Here we use lipid bilayer membrane as an example; **c** general scheme of conservation laws for both Diffusiophoresis and Marangoni effect

Fig. 3.

a Schematic of the discretized domain. The interface is discretized by the particles, represented by '*'. **b** The discontinuity of quantity f in the split element, where f could be tangential velocity $v_{\parallel}^{\pm*}$, pressure p^* or concentration/temperature c^*

Fig. 4.

a “Active” grid nodes within the computational tube and their corresponding particles on the interface. **b** Local approximation $\mathbf{r}^l(\xi^1)$ of interface around particle $\mathbf{y}_p$

Fig. 5.

General flow chart for the numerical solution. The Stokes flow and convection diffusion are solved via two solvers and the geometry and bending of the interface is tracked via the grid based particle method

Fig. 6.

a Schematic of a spherical vesicle moving in a long channel. **b** Geometries for the fluid and vesicle domains, as well as boundary conditions considered in the numerical solution

(a)

(b)

Fig. 7.

a Convergence of the errors with respect to the relative mesh size h/R , the errors converge to zero like $O(h^{2.1})$. **b** Convergence of the errors with respect to the timestep Δt , the errors converge to zero like $O(\Delta t^{1.9})$.

Fig. 8.

a Comparison between analytical solutions and modeling results for the velocity of vesicle at a given active flow. **b** Time evolution of the vesicle velocity. The velocity decreases gradually as local concentration gradient is decreased by convection-diffusion, a steady state is achieved and velocity plateaus. **c** The velocity and stress of fluid both inside and outside the vesicle. Fluid circulates inside the vesicle as a result of “stick” interface condition. Both the vesicle and the fluid are moving upwards. Note the pressure discontinuity across the vesicle surface due to surface tension

Fig. 9.

The dependence of steady velocity U_n on the relative size R/R_c . One could see that there exists a critical vesicle size $R/R_c \approx 0.5$, above which the steady velocity is decreased due to the effect of the channel

Fig. 10.

The shape of soft droplet at its steady state with different values of dimensionless parameter β , as well as how the velocity is affected by the shape. The droplet exhibits “pear-shaped” when surface tension is small and become circular when it is stiff. Vesicle is moving upwards in all cases due to the attraction between vesicle and solutes, while the “pear-shaped” soft vesicle moves slightly slower than the circular shaped rigid vesicle and the solute concentration field slightly varies accordingly

Fig. 11.

a Distribution of temperature **(a)**, pressure and streamlines **(b)** in the fluid domain at steady state. The pressure is lower at the upper edge of the vesicle due to the lower surface tension. The fluid outside the vesicle move downwards while the fluid inside circulates. The vesicle remains static with respect to far-field fluid; **c** the critical radius R_s of the vesicle for various temperature gradients and surface coefficients. The discrete symbols represent numerical results while the lines represent analytical results from [5]

Fig. 12.

Comparison between numerical result (*dots*) and analytical result (*line*). Good agreement is achieved for the steady velocity and the front-back asymmetry is gradually formed in the snapshots