Active colloids in the context of chemical kinetics

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Abstract
We study a mesoscopic model of a chemically active colloidal particle which on certain parts of its surface promotes chemical reactions in the surrounding solution. For reasons of simplicity and conceptual clarity, we focus on the case in which only electrically neutral species are present in the solution and on chemical reactions which are described by first order kinetics. Within a self-consistent approach we explicitly determine the steady state product and reactant number density fields around the colloid as functionals of the interaction potentials of the various molecular species in solution with the colloid. By using a reciprocal theorem, this allows us to compute and to interpret—in a transparent way in terms of the classical Smoluchowski theory of chemical kinetics—the external force needed to keep such a catalytically active colloid at rest (stall force) or, equivalently, the corresponding velocity of the colloid if it is free to move. We use the particular case of triangular-well interaction potentials as a benchmark example for applying the general theoretical framework developed here. For this latter case, we derive explicit expressions for the dependences of the quantities of interest on the diffusion coefficients of the chemical species, the reaction rate constant, the coverage by catalyst, the size of the colloid, as well as on the parameters of the interaction potentials. These expressions provide a detailed picture of the phenomenology associated with catalytically-active colloids and self-diffusiophoresis.
1. Introduction

The reduction in length scales brought about by lab-on-a-chip applications has raised a number of challenging issues. One of them is how to enable small objects to perform autonomous, directional motion (so-called self-propulsion) in a liquid environment [1–8]. For particles of micrometer size or smaller viscous and surface forces dominate the effects of inertia. Therefore, in order to achieve motion for them, new strategies have to be developed, which differ from those applicable for macroscopic objects [4, 5, 8, 9].

1.1. Active particles

Currently two main routes are followed towards this goal. The first one is based on mimicking the ingenious mechanical locomotion strategies of natural micro-organisms such as E. Coli or Spiroplasma [5]. These objects move by undergoing deformations of their bodies in a cyclic, non-reciprocal manner and by exploiting the anisotropy of the hydrodynamic drag. A thorough, extensive discussion of the developments in this area can be found in the recent reviews by Lauga and Powers [5], Elgeti, Winkler, and Gompper [10], Zöttl and Stark [11].

A promising alternative is that of employing catalytically activated chemical reactions to extract ‘chemical’ free energy from the surrounding liquid environment and to transform it into mechanical energy (i.e. motion of microparticles), resembling the way in which biological molecular motors function. One class of mechanisms to achieve this builds on ideas borrowed from classic phoresis, i.e. colloid motion in externally maintained gradients of certain thermodynamic fields [12]. The basic idea to achieve self-phoresis is to use particles which are partially covered by a catalyst in a well controlled way, designed such that symmetry breaking occurs and the particle is endowed with a ‘polar’ axis. The catalyst activates a chemical reaction in the surrounding solution [1, 8, 9, 13], generating gradients of reaction products across the surface of the colloidal particle. Owing to the solvent mediated, effective interactions between the reaction product molecules and the surface of the particle, within a thin interfacial layer a gradient in the osmotic pressure along the surface of the particle emerges. This leads to hydrodynamic flow of the solution around the particle and sets it into motion. Furthermore, in addition to the mechanical swimmers and chemically powered active colloids discussed here, self-thermophoresis [24] and photophoresis in combination with radiation-pressure [25] have recently been proposed as alternative self-propulsion mechanisms. (In the scenario above the requirement, that only a portion of the surface is catalytically active, is necessary for particles having axial- and fore-aft symmetry. For a shape missing the latter, self-phoresis may occur even if the whole surface of the particle is covered by catalyst. For example, for a uniform reaction rate (i.e. a constant flux of product molecules) across the surface of the particle,

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4 We note that there are also other mechanisms to convert chemical free energy into mechanical motion, such as electrochemical pumping employed by bi-metallic rods used in early experiments dealing with active colloids [2, 4, 14], thermally induced demixing of a binary liquid mixture near its critical temperature [15], or the ‘micro-jet-engines’ which rely on a bubble-pumping mechanism [6, 16–21]. At low Reynolds numbers, the latter has similarities with the mechanisms discussed theoretically in [22]. Yet another example is that of propulsion through pressure waves generated via catalyst activated chemical reactions in the surrounding fluid [23].
geometrical shape asymmetry is sufficient to induce an inhomogeneous number density of reaction products along the surface and therefore propulsion [26, 27].

Several proof-of-concept proposals of such chemically self-propelled objects, employing either self-phoresis [13, 14, 28–35] or bubble-pumping [6, 16, 17, 19–21] mechanisms, have already been successfully tested experimentally. Because of the intrinsic non-equilibrium character and due to the subtle combination of physics and chemistry behind this type of self-induced motility, many of the experimental [4, 6, 8, 14, 16, 20, 21, 31, 36] and theoretical [9, 36–42] studies have so far been focusing on systems which can be approximated as being unbounded. Recent experimental work has addressed new issues, such as improving the directionality of the motion against Brownian diffusion either by using external magnetic fields and paramagnetic core particles [16, 19, 21, 28, 32], or by exploiting the emergence of surface-bounded steady states of motion as they can occur in the vicinity of hard walls [71, 72], or by using a collection of chemically active particles as an artificial, non-biological system in order to study chemotaxis [30].

One interesting theoretical approach consists of describing an active particle in terms of an effective Langevin equation [76–81]. This has been, however, critically examined experimentally by Bocquet et al who have pointed out that in these out-of-equilibrium systems the notion of an ‘effective temperature’ and the mapping onto systems described by equilibrium statistical mechanics are problematic [82, 83]. The intriguing question concerning the extent to which similarities in collective behavior between active colloids and interacting Brownian particles can be captured by mappings with effective thermodynamic parameters has been recently scrutinized in [84]. This latter study established criteria under which certain models of ‘run-and-tumble’ particles are equivalent with the models of active particles developed in [76, 77]. However, it is important to note that in general, such systems cannot be described in terms of an equation of state [85, 86].

The hydrodynamic interactions between active swimmers have been shown to give rise to a rich behavior, such as synchronization of the swimmers [87, 88]. Accordingly, studies of simple models for the collective dynamics of active particles are enjoying considerable attention [45, 79, 80, 83, 89, 90].

Returning to the framework of ‘single-colloid’ systems and the emergence of self-phoresis, we note that a microscopic modeling of the processes in the interfacial region, explicitly taking into account the molecular structure of that region around a self-propeller, has been performed in [39, 40], and more recently in [91], by using molecular dynamics simulations. This approach allows one to keep track of the molecular details for all species at the expense, however, that only relatively small systems and short time scales can be accessed. A different strategy, pursued in [9, 37, 38, 41, 43, 92], is based on a continuum description of these active particles, transferred from the classical theory of diffusiophoresis [12]. Although this approach involves numerous assumptions, which are discussed in detail in [38, 41, 43, 92, 93], a qualitative agreement between the theoretical predictions and available experimental results has been reported [31, 32]. On the other hand, a strong sensitivity of the self-propulsion velocity even on tiny traces of salt in the solution [94] seems to indicate a more complex picture of the motion mechanism. Furthermore, for a ‘dimer’ model of an active particle (an active spherical colloid and an inert one of a different radius, connected via an infinitely thin rigid rod) quantitative agreement has been reported between this continuum description and the results of particle based numerical simulations [95]. Recently, a theoretical formulation of self-diffusiophoresis within the framework of classical non-equilibrium thermodynamics has been proposed [38, 93]. The influence of the details of the chemical reaction and of the

\[^{5}\text{See, however, the recent [43–53, 54–64, 65–75] which address the issue of confinement effects on self-propulsion.}\]
transport of the reactants and products on the emerging self-phoretic motion has also been studied recently [93, 96–99].

In the context of chemically active particles, the question of the detailed structure of the non-equilibrium steady-state density distributions around active particles, which is central to the present study, has been investigated in [39, 40], as well as recently in [93, 98, 100, 101]. Focusing on spherical colloids with catalytically active spherical caps, in [93, 100, 101] the number density fields have been calculated for various types of interactions (hard core, exponentially decaying, power law resembling van der Waals interactions). These calculations have been carried out as perturbation series in the Péclét number, which for these active colloids is typically small (see section 2), and in the range of the interactions between the reactive species and the colloid at which these are significant with respect to the thermal energy (e.g. more than a percent of the latter). These ranges are assumed to be short compared to the size of the colloid. (If this assumption does not hold, carrying out numerical simulations seems to be the only option available [93, 101].) In principle, this systematic expansion allows one to estimate the accuracy of the approximation caused by truncating the expansion at a certain order, but it has the drawback of a dramatic increase in the difficulty of obtaining closed form expressions beyond the first or second term in the expansion. For the dimer-sphere model with one catalytic sphere rigidly connected to an inert one, in [39, 40, 98] a Boltzmann-like ansatz was employed for the non-equilibrium distribution of reactants and products. The prefactor of these distribution was chosen to be the corresponding solution of the steady-state diffusion equation in the absence of interactions (other than the impenetrability of the active sphere) and with the surface of the catalytic sphere acting as a sink for the reactants and a source for the products. Under the assumption that the influence of the inert sphere on the diffusion is negligible, the reactant and product distribution profiles have been calculated. Obviously, in this case the accuracy of these approximations cannot be assessed intrinsically but only a posteriori via comparison with results from experiments or numerical simulations. For example, in [98] it has been shown that such approximate analytic results are in good agreement with data obtained from direct MD simulations. We note here, however, that as discussed in [42] it is important to account for the distortion of the density distributions due to the impenetrability of the inert sphere—in particular if the active sphere is only partially covered by catalyst and the two spheres do not touch—in order to fully understand how the inert sphere facilitates or hinders the emerging motion of the dimer.

1.2. Outline of the paper

Here we study in detail a mesoscopic model of an active colloid with a catalytic patch on its surface (see figure 1), so that the reactants, diffusing in a (chemically passive) solvent, react at this part of the surface by converting themselves into (diffusive) reaction products. The initial distribution of the reactants is taken to be homogeneous, but in the course of time and near the colloid a depletion zone for the reactants can emerge. We first focus on a simple reaction process in which a reactant \( A \) converts itself into a single product molecule \( B \), but further on we consider also the more general dissociation reaction \( A \rightarrow B + C \), in which two product molecules \( B \) and \( C \) emerge upon contact of an \( A \) molecule with the catalytic patch. We note that this latter process directly connects with, e.g. the dissociation of hydrogen peroxide into water and oxygen which has often been used in experimental realizations of chemically auto-motive particles (see, e.g. [4, 31, 34].)

We focus on understanding the steady-state structure of the number density fields of the product(s) and reactants near the active colloid by taking into account that reactants and products may have different diffusion coefficients and different interaction potentials with the
Distinct from the related previous approaches in [39, 40, 93, 98, 100, 101] discussed above, in order to calculate these non-equilibrium steady-state distributions we adopt an idea proposed previously and studied in the context of calculating chemical reaction rate constants [102]. By replacing therein the position dependent sink (for the reactant) and source (for products) boundary conditions on the surface of the active particle with certain effective ones, a completely analytical calculation of these steady-state density profiles can be carried out for quite general types of interactions between the diffusing species and the colloidal particle. These results allow us to compute that part of the force experienced by the colloidal particle which is solely due to the self-generated non-equilibrium spatial distributions of the reactive species. (We note that, on the other hand, the same interactions generate a force of the colloid acting on the reactive species which via their interaction with the solvent, encoded inter alia in the viscosity of the solution, transmit body forces acting on the solvent, inducing hydrodynamic flow and thus in turn a hydrodynamic force on the colloid (see, see section 4). At steady-state, and in the absence of external forces or torques acting on the colloid or on the fluid, this second part of the force experienced by the colloidal particle exactly cancels the first one, and therefore the net force on the colloid vanishes.) This part of the force can be used to calculate either the hydrodynamic flow of the solution (i.e. the pumping strength) induced by the active colloid (if the colloid is spatially fixed, e.g. by optical tweezers) or the velocity of the colloid, if the colloid is free to move. Our analysis is reliable as long as in the steady state the diffusion of the reactants and product molecules—here and in the following referred to also as ‘solute’—and the hydrodynamics in the system are such that the Péclet number (i.e. the ratio of the displacement

![Figure 1](image-url). An immobile spherical colloid of radius $R$ is centered and fixed at the origin $O$. A spherical cap with opening angle $\theta_0$ and centered around the point $D$ acts as a catalytic ‘patch’ on the surface of the colloid. The $z$-axis runs through $D$. $A$ and $B$ are the reactant and product molecules, respectively. In view of their low number densities, they are considered to be pointlike. The position vector $r$ with $|r| = r$ of a molecule $A$ forms an angle $\theta$ with the symmetry axis. The molecule $A$ has a distance $R$ from the surface of the colloid so that $r = r - R$. The solvent molecules are not shown; they form a homogeneous background acting as a heat bath. The solvent is passive with respect to the chemical reaction.
of the solutes due to convection to that due to diffusion) and the Reynolds number (i.e. the ratio of the inertial to the viscous contribution to the hydrodynamic flow of the solution) are small (see section 2). This implies that we disregard any change of the density distributions due to the flow of the solution. In this case, the diffusive and the convective (i.e. hydrodynamic) transport are effectively decoupled. The dependence of these quantities (i.e. the velocity of the colloid, if it is free to move, or the hydrodynamical pumping of the solution generated by an immobilized colloid) on the size of the colloid emerges naturally from the interplay between the reaction and diffusion constants, generalizing the results reported in [97, 105]. Therefore these results for the non-equilibrium spatial distributions of the reactive species—besides being of interest in their own right—can be immediately adopted in order to calculate the steady-state velocity of the self-propelled particle.

As a by-product of our analysis, in the case of triangular-well interaction potentials between the reactants and the colloidal particle we obtain several new results for effective reaction constants which, within the framework of the classical Smoluchowski theory of chemical kinetics [106], describe the reaction rates occurring at particles with inhomogeneous catalytic activity at their surface.

In the context of active particles, the detailed calculations and analyses noted above are motivated, inter alia by the following points:

• Most of the experimental studies of active particles have employed microscopy in order to trace the particle motion and to extract the corresponding velocity. However, carrying out such studies for a three-dimensional, bulk motion of active particles and determining their velocity \( V_{\text{free}} \) is very challenging. In section 4.3 we show that measurements of the stall force, e.g. by employing an optical trapping of the particle, provide the same information as the knowledge of the velocity \( V_{\text{free}} \) in the bulk. In section 4 the results of such measurements are related to detailed properties of the system, such as the coverage by catalyst, the interaction potentials between the particle and the molecular species, the rate of reaction, and the diffusion constants.

• In a stall configuration (‘pumping’, i.e. although the particle is motionless, the fluid is in motion because of the reactions at the surface of the particle and of the interactions between molecular species and the particle), the stall force is balanced by a contribution solely due to the interactions between molecular species and the particle and a hydrodynamic contribution due to the flow. The latter can be inferred eventually by mapping the flow around the particle using particle image velocimetry. If it is possible to independently map the distribution of chemical species around the immobilized colloid (see, e.g. [107]), the expressions for \( F_{\text{chem}} \) in sections 4.3 and 5 in connection with specific models for the interaction potentials allow one to estimate the parameters characterizing the potentials.

• If the interaction potentials between the various molecular species and the particle are known, measurements of the stall force for particles of different radii \( R \) provide the means, via the predicted dependence of the stall force on the radius (section 4), for a critical test of the model assumptions for the mechanism of reaction and motion. Furthermore, by repeating such experiment at various temperatures of the system, and thus eventually exploring the crossover regime between the kinetically-controlled and the diffusion-controlled ones, the confidence limits of the model can be tightened.

The outline of the paper is as follows. In section 2 we define our model for a translationally and rotationally immobile, chemically active colloid immersed in an unbounded system

\[6\] An analysis of the motion of a self-propelled colloid accounting for a non-zero Péclet number can be found in [103, 104].
with randomly dispersed diffusive reactants. Section 3 is devoted to calculate the stationary density profiles of mutually non-interacting $A$ (reactant) and $B$ (product) molecules around the immobile colloid with a reactive patch covering partly its surface. There we also describe the self-consistent approximation used to determine the coefficients in the expansions of the density profiles in terms of eigenfunctions. Extending our approach towards the general case of a dissociation reaction (such as, e.g. $A \rightarrow B + C$) is straightforward (see appendix B). In section 4 we first calculate $F_{\text{chem}}$—that part of the force exerted on the immobile colloid which is due to its molecular interactions with the solvent and the solute molecules (i.e. species $A$, $B$, etc), as well as that due to the hydrodynamic flow of the solution induced by the spatially non-uniform density profiles of the reactant and the products. Furthermore, by employing the reciprocal theorem in the presence of distributed body forces on the fluid [108, 109], we obtain an explicit expression for the self-propulsion velocity $V$ of the colloid if it is free to move. Moreover we also derive an explicit expression for the stall force necessary to immobilize the active colloid which otherwise would move freely. In section 5 these results are discussed further for the particular case of triangular-well interaction potentials. There, we present explicit expressions for the chemical force, the stall force, and the self-propulsion velocity as functions of the parameters of the triangular-well interaction potentials, the diffusion coefficients, the radius of the colloid, the size of the catalytic patch, and the chemical rate constants. The dependences on these parameters are discussed in detail and we highlight several counter-intuitive effects, such as that (i) for certain parameters $F_{\text{chem}}$ and $V$ may have different signs; (ii) $V$ is a non-monotonic function of the value of the interaction potential at the surface of the colloid, and (iii) the maximal self-propulsion velocity, as function of the size of the catalytic patch, is in general attained at coverages by catalyst being smaller than one half. We summarize the results in section 6 along with our conclusions. Certain important derivations are collected in the appendices A–D. In appendix E we provide a summary of our notations which is meant to ease following the text.

2. Model

We consider a macroscopically large reaction bath of volume $V$ in which a spherical colloidal particle of radius $R$ is immersed. We choose the origin of the coordinate system to be at the center of the colloid (see figure 1). We consider two situations: either an immobile colloid (e.g. held by an optical tweezer or a very thin tethered spring), or an unconstrained colloid which at steady state moves with velocity $V$ through the solution. (In the absence of thermal fluctuations, due to the axial symmetry of the system the axis of the colloid does not rotate.) In the latter case, the coordinate system is attached to (and thus co-moving with) the colloid. The reaction bath consists of solvent molecules $S$, reactant molecules $A$, diffusing with diffusion coefficient $D_A$, and (after some time) product molecules $B$, diffusing with diffusion coefficient $D_B$. The reactant molecules $A$ (molecular mass $m_A$), the product molecules $B$ (molecular mass $m_B$), and the solvent molecules (molecular mass $m_S$) are much smaller than the colloid, so that the solution can be approximated as a continuum, apart from density oscillations in the molecular vicinity of the colloid surface. The number densities (number of molecules per volume) of $A$ and $B$ molecules are taken to be very small compared with the number density of the solvent; therefore we assume that there are no $AA$, $BB$, and $AB$ interactions. The interactions between the $A$ ($B$) molecules and the solvent are encoded, together with those among the solvent molecules, inter alia in the viscosity $\mu$ of the solution treated as a continuous medium; they enter as well, e.g. via the Stokes-Einstein relation, into the corresponding diffusion coefficient $D_A$ ($D_B$). The solution is assumed to behave as an incompressible, Newtonian fluid.
A spherical cap of the surface of the colloid particle, lying within the angular region $0 \leq \theta \leq \theta_0$ centered around $D$ (see figure 1), has the following ‘catalytic’ properties: As soon as an $A$ molecule approaches the surface of the colloid at any point belonging to the catalytic patch (CP), within a minimal distance $a$ (where $a \ll R$ is of the order of the size of the $A$ molecule), it undergoes with probability $p$ an irreversible reaction (conversion) into a product molecule $B$:

$$A + \text{CP} \xrightarrow{p} B + \text{CP}. \quad (1)$$

The probability $p$ characterizes the elementary reaction act: $p = 0$ means that no reaction occurs, while for $p \to 1$ one has a ‘perfect’ reaction, i.e. $A$ turns into $B$ upon any encounter with the surface. We assume that the catalyst is neither consumed by the reaction in equation (1), nor temporarily ‘passivated’ by an intermediate product, and thus at any time it can participate actively in an unlimited number of chemical transformations. The solvent, acting as a heat bath, serves as a source or a sink of heat if the catalytic reaction is endothermic or exothermic, respectively. For reasons of conceptual clarity, we consider only the case that all species in the solution ($S, A, B$, etc.) are electrically neutral. The extension to the case of ionic species, which requires to consider charge conservation and its coupling to mass transport, eventually can be treated similarly to the cases discussed in, e.g. [92–94, 100].

In what follows we shall also consider a more general reaction scheme, corresponding to a catalytically induced dissociation reaction of the form

$$A + \text{CP} \rightarrow B + C + \text{CP} \quad (2)$$

in which the reactant $A$, upon contact with the catalytic patch, breaks up into a pair of products $B$ and $C$ (with the latter two, in the general case, being different from the solvent molecules) created at a certain distance apart of each other. The diffusion coefficient of the $C$ molecules will be denoted as $D_C$. Such a reaction is inspired by Pt-catalyzed dissociation of hydrogen peroxide into water and oxygen molecules, which has been used in many experimental realizations of self-propelling particles [96]. In the case of peroxide decomposition, if the solvent $S$ is water the product molecules $C$ are also water molecules so that the reaction produces excess solvent. The excess amount of solvent, which emerges in the course of this reaction is small because it is controlled by the concentration of $A$ molecules (hydrogen peroxide) which is small. In this particular case the reaction scheme in equation (2) reduces to the simpler one in equation (1).

The initial state of the system, i.e. before the immersion of the chemically active colloid (or before switching on its catalytic activity), is that of a well stirred reaction bath: the $A$ molecules are uniformly distributed within the reaction bath with mean number density $n_{00}^A = n_0$. (But in the course of time, upon turning on the reaction, a non-uniform concentration profile can emerge.) Initially the $B$ molecules are absent in the system. The bath is in contact with a reservoir of $A$ molecules which maintains this density $n_{00}^A = n_0$ at distances far away from the colloid at all times. We furthermore assume that the reaction bath is also in contact with a perfect sink of $B$ molecules so that $n_{0}^B = 0$ far away from the colloid at all times; together with the reservoir for $A$ molecules, this ensures that a steady state can be maintained in the bath if the reaction is active. As mentioned before, the mean number densities of the $A$ and $B$ molecules are assumed to be, at all times, much smaller than the mean number density $n_{00}^S$ of the solvent molecules; therefore the latter is assumed to be at all times approximately equal to its initial value $n_{00}^S$ before the reaction is turned on. The colloid is impermeable to any of the molecules ($A, B$, or $S$) in the mixture.
The solvent molecules interact among themselves and with the $A$ and $B$ molecules. As noted above, these interactions are, *inter alia*, accounted for by the viscosity $\mu$ of the mixture and by the diffusion constants $D_A$ and $D_B$. They also interact with the colloid via a radially symmetric interaction potential $\Phi_S(r)$ (per molecule of solvent), in addition to the hard core repulsion accounting for the impermeability of the colloid. Due to the spherical symmetry, for a molecule located at $r$ this distance from the colloid is given by $\tilde{r} = r - R$ (see figure 1) and thus for convenience we introduce the radially symmetric potential $\Phi_S(r) := \Phi_S(r - R)$. We account for the hard-core repulsion via $\Phi_S(r < R) = \infty$. (Note that in the latter condition the molecules are implicitly treated as point-like particles because of their size being much smaller than $R$.) As already noted in the Introduction, we assume that the solvent is passive with respect to the reaction and that it acts as a macroscopic heat bath, which keeps the temperature constant even in the presence of the reactions.

Similarly, the $A$ and $B$ molecules interact with the colloid via an interaction potential $\Phi_{ab}(\tilde{r})$ (per molecule), respectively, in addition to the hard core repulsion which makes the colloid impermeable for the molecules in the mixture. We introduce the radially symmetric potentials $\Phi_{ab}(r) := \Phi_{ab}(r - R)$ and account for the impenetrability of the colloid via $\Phi_{ab}(r < R) = \infty$. Thus we disregard the possibility that the catalytic patch introduces an angular dependence on $\theta$ of any of the interaction potentials $\Phi_{ab}(r)$ between the molecules and the colloid, as well as the influence of the eventual size disparity between the three types of molecules on the location of the ‘hard wall’ surface of the colloid (see also the succinct discussion below). For reasons of having simple notations later on (see section 3), we also introduce here the interaction potentials of the $A$ and $B$ molecules with the colloid relative to the corresponding potential for the solvent molecules weighted by the ratio of the mass of the $A$ ($B$) molecules to the mass of the solvent molecules (see appendix A):

$$W_{ab} := \frac{m_A}{m_S} \Phi_{ab}(r) - \frac{m_B}{m_S} \Phi_{ab}(r), \quad r > R. \quad (3)$$

For the case of the reaction in equation (1), mass conservation obviously requires $m_A = m_B$. However, in order to keep the formulation consistent with the more general reaction processes, involving more than one species of product molecules, which are considered later on, we maintain the labels $A$ and $B$ even for this simple case.

Before proceeding with the analysis of the dynamics of the system, it is important to clarify the choice of the position of the hard wall. In general this is a complicated issue for interfaces involving more than two molecular species. Additionally, the divergences of the interaction potentials (and of their derivatives) caused by molecular hard cores in the limit $\tilde{r} \to 0$ significantly complicate the mathematical arguments given below (see section 3). This leads us to use the following approach. Within a point-particle description of all molecular species, the radius $R$ of the colloid, and thus the position of the hard wall, is fixed by the most outward layer of molecules composing the colloid. We assume that each of the molecular pair interactions between a molecule from the colloid and a molecule of species $j$ ($j = A, B, S$) is described well by a Lennard-Jones 6–12 potential. This involves the parameters $\sigma_j$ (corresponding to the molecular diameter) and $\epsilon_j$ (corresponding to the characteristic energy, in units of the thermal energy $k_B T$, where $k_B$ denotes the Boltzmann constant and $T$ the absolute temperature), and leads to the ‘exact’ interaction potentials $W_j(r)$ which (all of them) diverge as $r \to R$. Subsequently, the radius $R$, and therefore the position of the hard wall, is redefined as $R \to R + \epsilon$, with $0 < \epsilon \ll R$ of the order of a molecular size. These truncated potentials are bounded at $r = R$ (with $R$ interpreted as the shifted radius), at the expense that $W_j(R)$ now turn into phenomenological, effective parameters, and that the results depend on the choice of $\epsilon$. 


The arbitrariness can be reduced by further modifying the shape of the potentials \( W_j(r) \), e.g., by adjusting the point at which their tails are truncated while requiring that the excess adsorption of each component, which is an experimentally measurable quantity, is the same for the shifted and modified potentials and for the exact ones. On one hand this does not eliminate the dependence on the choice of \( \epsilon \), on the other hand it provides a prescription based on which, in principle, this dependence can be explored systematically. While this approach cannot be justified rigorously, we note that such a procedure has been employed recently with satisfying results for describing equilibrium properties, such as phase coexistence and interfacial properties, by using triangular-well potentials, ‘mimicking’ (in the above sense) Lennard-Jones interactions [110–112].

Focusing on the reaction scheme given in equation (1), the goal is to determine the spatial distributions of the \( A \) and \( B \) molecules once a steady state has been attained and to study the resulting chemical force \( \mathbf{F}_{\text{chem}} = \mathbf{F}_{\text{chem}}(\theta_0, \Delta D, D_B, R, p; [W_A, W_B], \mu) \) exerted on the inhomogenously distributed \( A \) and \( B \) molecules, the velocity \( \mathbf{V} \) (as a function of the same parameters) if the colloid is free to move, and the stall force \( \mathbf{F}_{\text{ext}} \) necessary to immobilize a freely moving colloid. (It is straightforward to consider the more general dissociation reaction in equation (2); therefore we shall merely present the corresponding results without providing their derivation.)

3. Steady state distribution of reactant and product molecules

Within the framework of the classical theory of linear non-equilibrium thermodynamics [93, 101, 113, 114], and under the assumptions of small number densities, negligible cross-diffusion, and small Péclet numbers of the \( A \) and \( B \) molecules, the dynamics of the number density distributions are governed by the diffusion equations (see appendix A)

\[
\frac{\partial n_j}{\partial t} = D_j \nabla \cdot [e^{-\beta W_j(r)} \nabla (e^{\beta W_j(r)} n_j)], \quad j = A, B. \tag{4}
\]

At steady state, the time derivatives in equation (4) are zero, and the resulting partial differential equations are to be solved subject to appropriate boundary conditions.

The coordinate system (see figure 1) is chosen such that the \( z \)-axis passes through the center of the patch (point \( D \)). The system exhibits azimuthal symmetry around the \( z \)-axis and therefore the densities \( n_{A,B}(r,t) \) of the \( A \) and \( B \) molecules, respectively, are independent of the corresponding azimuth angle \( \phi \) around the \( z \)-axis.

3.1. Steady state distribution of the reactant

In terms of spherical polar coordinates and by dropping the dependence on the azimuthal angle \( \phi \), one finds that at steady state the number density \( n_A \) of the reactant \( A \) molecules fulfills (see equation (4))

\[
0 = \frac{D_A}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial n_A}{\partial r} \right) + \frac{\beta D_A}{r^2} \frac{\partial}{\partial r} \left( r^2 n_A \frac{\partial W_A}{\partial r} \right) + \frac{D_A}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial n_A}{\partial \theta} \right). \tag{5}
\]

where \( \theta \) is the polar angle measured with respect to the \( z \)-axis (see figure 1). For equation (5) to be well defined for all \( r > R \) we restrict our analysis, as discussed in section 2, to interaction...
potentials \( W_A(r) \) which are finite for all \( r > R \), have a finite first derivative for all \( r > R \), and vanish sufficiently fast as \( r \to \infty \) (see section 4).

Equation (5) is to be solved subject to the boundary condition

\[
n_A\big|_{r=\infty} = n_0,
\]

which stipulates that the solute number density \( n_A \) approaches the reservoir number density \( n_0 \) for \( r \to \infty \), and subject to an effectively reflective boundary condition valid at the non-catalytic part of the surface of the colloidal particle \( (r = R, \, \theta_0 < \theta \leq \pi) \):

\[
J_A := -D_A \left( n_A' + \beta n_A W_A' \right)_{r=R} = 0, \quad \theta_0 < \theta \leq \pi,
\]

where \( J_A := e_r \cdot J_A \) denotes the radial component of the current of \( A \) molecules at the point \( \theta \) on the surface \( r = R \) of the particle, \( W_A = dW_A/dr \), and \( n_A' = \partial n_A(r, \theta, t)/\partial r \) (see equation (4)), with the convention that all the evaluations at \( r = R \) are interpreted as evaluating at \( r = R + \varepsilon \to R \).

Next we turn to the boundary condition at the catalytic part of the colloid surface which accounts for the conversion of \( A \) molecules into \( B \) molecules. Under general conditions such a conversion can be taken into account by requiring that at any point within the area of the catalytic patch \( (r = R, 0 \leq \theta \leq \theta_0) \) the current of \( A \) molecules normal to the surface equals the rate of their annihilation due to the chemical reaction, i.e. by imposing the so-called radiation [122] (or imperfectly absorbing) boundary condition

\[
J_A := -D_A \left( n_A' + \beta n_A W_A' \right)_{r=R} = -\kappa n_A|_{r=R}, \quad 0 \leq \theta \leq \theta_0,
\]

where \( \kappa > 0 \), such that the right hand side has the proper meaning of an ‘annihilation’ term. (equation (8) can be alternatively interpreted as a current ‘into the particle’ on the left-hand side (lhs), thus reducing the number density of \( A \) species in solution, which is given by \( \kappa n_A \) on the right-hand side (rhs.).) Note that in equation (8) \( j_A \) varies as function of \( \theta \). Before proceeding it is useful to comment on the proportionality factor \( \kappa \) (with the units of length/time). This factor can be expressed [123] as the ratio of the elementary reaction act constant \( K \) (volume times number of acts per unit of time within this volume) and the surface area of the catalytic patch:

\[
\kappa = \frac{K}{4\pi R^2 f_g},
\]

where \( f_g = f_g(\theta_0) = \sin^2(\theta_0/2) \) is the so-called geometric steric factor characterizing the fraction of the surface of the particle covered by the catalytic patch. In turn, the elementary reaction act constant is given by \( K \equiv W_0 V_a \) [123], where \( W_0 \) is the rate describing the number of reaction acts per unit of time within the volume \( V_a \) of the reaction zone. In the present system the reaction occurs within a segment of a spherical shell given by \( R \leq r \leq R + a \) and \( 0 \leq \theta \leq \theta_0 \) with \( a \) the minimal distance (figure 1). This volume is \( V_a = 4\pi R^2 a f_g, a \ll R \). Thus the proportionality factor is given by

\[
\kappa = W_0 a
\]

and is independent of \( \theta_0 \). Via \( W_0 \) this factor depends, however, on the probability \( p \) of the \( A \to B \) conversion because \( W_0 \propto p/(1 - p) \tau \), where \( \tau \) is a typical time spent by an \( A \) molecule within the reaction zone [124]. (A full equation for \( W_0 \) is not available.) This implies that for \( p = 0 \) (i.e. no reaction) one has \( \kappa = 0 \) and the rhs of equation (8) vanishes, i.e. in this limit the reflecting boundary condition for the normal current is recovered. For \( p \to 1 \) (i.e. the
reaction is perfect and \( A \) turns into \( B \) upon any encounter with the surface) one has \( \kappa \rightarrow \infty \).
Since we have assumed that the gradient of the interaction potential is bounded for \( r \rightarrow R \), the lhs of equation (8) is bounded. This can be reconciled with \( \kappa \rightarrow \infty \) on the rhs only if in this limit \( n_A|_{r=R} \rightarrow 0 \) such that \( 0 < \kappa n_A|_{r=R} < \infty \). Thus in this limit one finds the perfect sink boundary condition. For \( \kappa < \infty \) (i.e. \( p < 1 \)), the boundary condition in equation (8) is therefore equivalent to the physical assumption that not all encounters of the \( A \) molecules with the catalytic part of the surface of the colloid lead to a reaction event.

For systems which are catalytically active as a whole (i.e. \( \theta_0 = \pi \)) and in the absence of the interaction potential (apart from the hard-core repulsion) between the colloid and the \( A \) molecules, such a boundary condition has first been proposed by Collins and Kimball [122] (see also [125]) as a generalization of the conventional Smoluchowski theory [106] which stipulates a perfect sink boundary condition. Furthermore, for \( \theta_0 = \pi \) an exact calculation of the steady-state diffusion problem defined by equations (4), (7) and (8) is possible for quite general forms of the interaction potential \( W_A(r) \) as well as for a spatially varying diffusion constant \( D_A(r) \) [126, 127].

In the absence of interactions (apart from the hard-core repulsion) between the colloid and the \( A \) and \( B \) molecules, the solution of the diffusion equation (equations (5)–(8)) subject to such mixed boundary conditions (i.e. different boundary conditions are used on different parts of the boundary of the domain of the equation) has been studied by several groups in the past. This started with the seminal work by Solc and Stockmayer [128, 129], who developed an approximate method to treat this mathematical problem. (For this case of \( W_{A,B} = 0 \), also several other approximations have been proposed (see, e.g. [123, 129, 130]).) Moreover, an exact solution based on the so-called dual series relations is available [131, 132]. However, this procedure is not only cumbersome, but it also does not render a transparent, analytical form of the solution and thus masks the physical content of the results.

In what follows we resort to an approximate approach as the one proposed in [102]. This choice is motivated by the fact that the approach developed in [102] is rather straightforward and is known to yield—in the absence of interactions—results which are in a good agreement with numerical solutions of the original problem [131]. Here, we generalize this approach by taking into account the interactions between the molecules and the colloid, which are absent in the original work [102]. As a byproduct of our analysis, this allows us to obtain several new results concerning the effective reaction constants and density profiles for systems with heterogeneous reactivity in the presence of interaction potentials.

In accordance with [102], the boundary condition in equation (8) is replaced by

\[
-D_A(n_A' + \beta n_A W_A)|_{r=R} = -Q, \quad 0 \leq \theta \leq \theta_0,
\]

where \( Q > 0 \) is a ‘trial’ constant, independent of \( \theta \), which is determined self-consistently by requiring that the former condition given by equation (8) holds only on average over the region \( 0 \leq \theta \leq \theta_0 \) of the catalytic patch, i.e.

\[
D_A \int_0^{\theta_0} d\theta \sin \theta (n_A' + \beta n_A W_A)|_{r=R} = \kappa \int_0^{\theta_0} d\theta \sin \theta n_A(R = R, \theta).
\]

Equations (12) and (11) imply (see also equation (8))

\[
Q (1 - \cos \theta_0) = \kappa \int_0^{\theta_0} d\theta \sin \theta n_A(R, \theta).
\]

Since via equation (11) \( n_A(R, \theta) \) depends on \( Q \), equation (13) represents an implicit equation for \( Q(\kappa) \) (see below).
We seek the solution of equation (5), which is the steady-state solution of equation (4), via the ansatz
\[ n_a(r, \theta) = n_0 e^{-\beta W_a(r)} \left[ 1 + \sum_{n=0}^{\infty} a_n g_n(r) P_n(\cos \theta) \right], \tag{14} \]
where \( a_n \) are dimensionless coefficients to be determined from the boundary conditions and \( P_n(\cos \theta) \) is the Legendre polynomial of order \( n \). We note that the first term on the rhs of equation (14) is the equilibrium Boltzmann distribution of \( A \) molecules around the colloid (see equation (6)), e.g. in the absence of the chemical reaction or for an infinitely fast diffusion of \( A \) molecules (i.e. \( D_A = \infty \)) in which case all coefficients \( a_n \) vanish (see below). Therefore the second term represents the whole out-of-equilibrium contribution to the concentration distribution due to the chemical reaction and due to a finite value of the diffusion constant \( D_A \) of the \( A \) molecules.

Upon inserting equation (14) into equation (5), one finds that the former is the solution of the latter if the functions \( g_n(r) \) solve
\[ g_n''(r) + \left( \frac{2}{r} - \beta W'_a(r) \right) g_n'(r) - \frac{n(n+1)}{r^2} g_n(r) = 0. \tag{15} \]
Moreover, in order that \( n_a(r, \theta) \) given by equation (14) satisfies the boundary condition in equation (6), the solutions \( g_n(r) \) of equation (15) are subject to the boundary condition that they vanish for \( r \to \infty \). For each \( n \) the solutions \( g_n(r) \) of equation (15) are defined up to multiplicative constants. Without loss of generality, as explained below, we fix these constants by choosing the normalization \( g_n(r = R) = 1 \). This renders the coefficients \( a_n \) to be unique.

For \( n = 0 \), from equation (15) one finds
\[ g_0(r) = R_D \int_r^\infty \frac{e^{\beta W_a(u)}}{u^2} \, du \tag{16} \]
with \( g_0(r \to \infty) = R_D/r \), where \( R_D \) is related to the so-called Debye radius (see [133]):
\[ R_D = \left( \int_r^\infty \frac{du \, e^{\beta W_a(u)}}{u^2} \right)^{-1} \tag{17} \]
note that \( R_D = R \) for \( W_a = 0 \). For \( n \geq 1 \), equation (15) cannot be solved analytically for a generic interaction potential \( W(r) \). However, for \( r \to \infty \) the interaction potentials of interest for our system decay \( \sim 1/r \) or faster so that \( \beta W'_a(r) \ll 1/r \) for \( r \gg R \). Accordingly, at large distances \( r \gg R \) equation (15) reduces to the differential equation satisfied by the radial functions of the Laplace equation. This ensures that for any \( n \geq 1 \) equation (15) admits a solution \( g_n(r) \) with the asymptotic behavior \( g_n(r \gg R) \sim r^{-n+1} \) and thus obeys the boundary condition to vanish for \( r \to \infty \).

Combining the boundary conditions in equations (7) and (11) and inserting therein the expansion given by equation (14) leads to
\[ \sum_{n=0}^{\infty} a_n g_n'(R) P_n(\cos \theta) = \frac{Q e^{\beta W_a(R)}}{D_A n_0} \Theta(\theta_0 - \theta), \tag{18} \]
where \( \Theta(x) \) is the Heaviside step function (\( \Theta(x) = 1 \) for \( x \geq 0 \) and zero otherwise). Multiplying both sides of equation (18) by \( (\sin \theta) P_n(\cos \theta) \), integrating them over \( \theta \) from 0 to \( \pi \), and using the orthogonality of the Legendre polynomials one obtains
\[ a_n = \frac{Q e^{\beta n_0(R)}}{2 D_n n_0} \frac{\phi_n(\theta_0)}{g_n^R(R)}, \quad n \geq 0, \]  

(19)

where

\[ \phi_n(\theta_0) = P_{n-1}(\cos \theta_0) - P_{n+1}(\cos \theta_0), \quad n \geq 0, \]  

(20)

with the convention \( P_1(\cos \theta_0) = 1 \). We note that because \( a_n \sim 1/g_n^R(R) \), one has \( a_0 g_0 \sim g_0^R g_0^R \).

Thus in the final result in equation (14) the normalization amplitude of \( g_n \) drops out and \( a_0 \) is independent of the choice for this normalization, as it should.

After substituting \( a_n \) from equation (19) into equation (14), inserting the resulting expression into equation (13), and taking advantage of the relation

\[ \phi_0(\theta_0) = (2n + 1) \int_0^{\theta_0} d\theta \sin \theta P^2(\cos \theta), \]  

(21)

one finds the following explicit expression for \( Q \):

\[ Q = \frac{4 \kappa n_0 D_n e^{-\beta n_0(R)\phi_0(\theta_0)}}{4 D_n \phi_0(\theta_0) - \kappa \sum_{n=0}^{\infty} \frac{\phi_{n+1}(R)}{(n+\beta)^2}}. \]  

(22)

where \( \phi_0(\theta_0) = 1 - \cos \theta_0 = 2 \sin^2(\theta_0/2) \). In the following, due to the normalization choice for the functions \( g_n(r) \) the ratio \( g_n(R)/g_n^R(R) \) inside the sum will be replaced by \( 1/g_n^R(R) \). This concludes the calculation of the distribution \( n_A(r, \theta) \) of reactant molecules (equations (14), (15), and (19)–(22)).

Upon closing this section we emphasize that within the expansion in equation (14) the radial and angular forms of the functions are exact. Only the coefficients \( a_n \) are determined approximately, using a generalized self-consistent approach [102]. In the following, we shall evaluate the contributions to the force \( F_{chem} \) exerted on the immobile colloid (and, if it is free to move, to its velocity \( V \)) stemming from the interactions of the colloid with the \( A \) molecules, the spatial distribution of which is given by equation (14) with the coefficients \( a_n \) defined by equations (19) and (22) (and similarly due to the interactions with the \( B \) and \( C \) molecules, the distributions of which will be determined in section 3.3 and appendix B). To this end, one has to integrate the distribution in equation (14) multiplied by the gradient of the interaction potential in order to determine \( F_{chem} \) and multiplied by the gradient of the interaction potential and by the axially symmetric part of the velocity field in order to calculate \( V \), which will be carried out in section 4. We proceed by showing that the contributions to \( F_{chem} \) and \( V \) due to the interactions of the colloid with the \( A \) molecules are given by \( F_{chem} = (4\pi n_0/3) \alpha J_A \) and \( V = (2n_0/\mu R) n_0 J_A \), where \( I_A \) and \( J_A \) are exact functional expressions of the interaction potentials and only the coefficient \( \alpha \), which due to the symmetry of the system is the only relevant one, is determined approximately.

The accuracy of the approximation for the coefficient \( \alpha \) can be estimated from the following simple argument. Suppose that one is able to solve the mixed boundary problem defined by equations (5)–(8) exactly, and hence, to obtain the exact expressions for the expansion coefficients \( a_0 \) in equation (14). Then, inserting this expansion into equation (8), multiplying both sides by \( \sin(\theta) \cos(\theta) \) and integrating over \( \theta \) from 0 to \( \pi \) (recall that \( j_1 \equiv 0 \) for \( \theta_0 < \theta \leq \pi \)), one obtains the following relation between the exact coefficient \( \alpha_1 \) and the exact current \( j_A \) (which in general is a function of \( \theta \)):

\[ \alpha_1 = -\frac{3}{4} \frac{e^{\beta n_0(R)}}{n_0 D_n g_n^R(R)} \int_0^{\theta_0} j_A(2\theta) d\theta. \]  

(23)
On the other hand, the relations in equations (19) and (21) provide the following approximate expression for $a_1$:

$$
a_1 = \frac{3}{4} \frac{e^{\beta W_0(R)}}{n_0 D_A g'_0(R)} \int_0^{\theta_0} \sin(2\theta) d\theta. \quad (24)
$$

Therefore the accuracy of estimating the coefficient $a_1$ via using the self-consistent approach [102] turns out to be the same as the one associated with approximating the integral on the rhs of equation (23) as

$$
- \int_0^{\theta_0} j_A \sin(2\theta) d\theta \approx Q \int_0^{\theta_0} \sin(2\theta) d\theta. \quad (25)
$$

On physical grounds, one may expect that $j_A$ depends very weakly on $\theta$ within the interior part of the catalytic patch away of its periphery. Hence, for the major part of the integration interval the current $j_A$ will factor out from the integral rendering equation (25) to be an equality (compare with equations (8) and (11)). An appreciable dependence of the current on $\theta$ may appear only in the vicinity of $\theta = 0$ and $\theta = \theta_0$, where $j_A$ drops to zero. Therefore one can expect that the self-consistent approximation in [102] will provide an accurate estimate for $a_1$ provided that $\theta_0$ is not too small. Remarkably, even in the limit $\theta_0 \to 0$, in which one may expect the most significant deviations, the self-consistent approximation is surprisingly reliable, as evidenced by the numerical analyses in [131] and more recently in [134], which studied the so-called narrow escape problem in the presence of long-ranged interactions with the confining boundary using essentially the same approximate approach as the present one. It was shown in [134] that the self-consistent approximation captures adequately even the dependences of those terms, which dominate in the limit $\theta_0 \to 0$, on all pertinent parameters and it only slightly underestimates the numerical factors.

Finally, in section 5 we shall show that for the particular case $\theta_0 = \pi/2$ (i.e. for the so-called Janus colloids) and for short-ranged triangular-well interaction potentials, our general results reproduce the known limiting forms of the self-propulsion velocity as obtained in [97] within an approach based on the concepts of the effective Derjaguin length and the phoretic slip.

### 3.2. Chemical kinetics interpretation: effective reaction constants

In order to translate our results into the usual nomenclature of chemical kinetics, we follow [102, 126] and introduce an ‘effective’ reaction constant $K_{\text{eff}}$, which accounts for the combined effect of the nonzero reaction probability at the catalytic patch and the diffusive transport of the reactants to the patch. $K_{\text{eff}}$ is defined as the number of $A$ molecules, which are distributed according to $n_A(r, \theta)$ and which would flow, per time, through the surface $r = R$ if the colloid was permeable, divided by $n_0$. Using equations (7), (8) and (12) this takes the form

$$
K_{\text{eff}} = \frac{2\pi R^2 D_A}{n_0} \int_0^\pi d\theta \sin \theta \left[ n'_A + \beta n_A W'_A \right]_{r=R} = \frac{2\pi R^2 \phi_0(\theta_0)}{n_0} Q. \quad (26)
$$

We note that the coefficients $a_n$ in equation (19) can be expressed in terms of this effective reaction constant as

$$
a_n = \frac{K_{\text{eff}}}{K_S} \frac{e^{\beta W_0(R)}}{R g'_0(R)} \frac{\phi_0(\theta_0)}{\phi_0(\theta_0)} \quad n \geq 0, \quad (27)
$$
where $K_S = 4\pi D_A R$ is the Smoluchowski constant [106]. $K_{\text{eff}}$ and $K_S$ have the units of volume per time, as $K$ does.

By replacing $Q$ with the expression in equation (22), and by noting that equation (16) implies $R_D = -R^2 g'_0(R)e^{-\beta W_A(R)}$, equation (26) can be cast into the physically intuitive form

$$\frac{1}{K_{\text{eff}}} = \frac{1}{K^*} + \frac{1}{K_S f_{dc}(\theta_0)}, \quad (28)$$

where $dc$ stands for diffusion controlled. The Smoluchowski–Debye constant $K_{SD}$ [133] (compare equation (17))

$$K_{SD} = 4\pi D_A R_D \quad (29)$$

equals the flux (divided by $n_0$) of diffusive molecules, the density of which at $r \to \infty$ is kept fixed and equal to $n_0$, through the hypothetical surface of an immobile, perfectly absorbing sphere interacting with the molecules via a radially symmetric potential $W_A(r)$. The quantity

$$K^* = 2\pi R^2 \phi_0(\theta_0) \kappa e^{-\beta W_A(R)}$$

$$= 4\pi R^2 f_\kappa \kappa e^{-\beta W_A(R)} = K e^{-\beta W_A(R)} \quad (30)$$

is an effective constant for an elementary reaction act factored into a term $K$ (see equation (9)), which depends only on the reaction kinetics $\kappa$ and the geometry (via $\theta_0$) of the catalytic patch, and a term which depends only on the interaction potential. In the diffusion-controlled limit $K^* \to \infty$ (in the sense that $K^* \gg K_S f_{dc}(\theta_0)$, but not necessarily infinitely large, see below), the quantity

$$f_{dc}(\theta_0) = 2\phi_0^2(\theta_0) \left( \frac{g_0(R)}{\phi_0^2(\theta_0)} \sum_{n=0}^{\infty} \frac{1}{(n+1/2)g_0(R)} \right) \quad (31)$$

plays the role of an effective steric factor: it shows how the reaction rate in equation (29) is reduced effectively due to the fact that the catalytic patch occupies only some part of the colloid surface. As will be seen below, it shows a different angular behavior as compared with the purely geometric steric factor $f_g = \sin^2(\theta_0/2)$. We emphasize that the full functional form of $W_A(r)$ enters both into $K_{SD}$ (see equations (29) and (17)) and into $f_{dc}$ (via $g_0(r)$; see equations (31) and (15)) whereas $K^*$ depends only on $W_A(r = R)$ (equation (30)). (Here we recall that the argument $r = R$ must be interpreted as $r = R + \epsilon \to R$ and that we assume the potential and its derivatives to be bounded at $r = R + \epsilon$.)

Equation (28), which resembles the law of addition of inverse resistances, bears out the combined effect of two rate-limiting steps: the random, diffusive search of the A molecules for the catalytic patch and the subsequent elementary reaction act. Such a form allows one to distinguish easily between the so-called diffusion-controlled limit, in which the time needed by the A molecule to diffuse to the catalytic patch is the rate-limiting step (with the elementary reaction contribution $1/K^*$ itself being negligible in comparison), and kinetically-controlled reactions for which the opposite holds, i.e. $K^* \ll K_S f_{dc}(\theta_0)$. In the following, we shall denote this limit symbolically as ‘$D_A \to \infty$’, which does not imply, however, that $D_A$ is infinitely large, but it only means that the latter inequality holds.

One can readily check that in the absence of interaction potentials, i.e. for $W_A(r) \equiv 0$, the result in equation (28) reduces to (see equation (30))

$$\frac{1}{K_{\text{eff}}} = \frac{1}{K} + \frac{1}{K_S f_{dc}(\theta_0)}, \quad (32)$$
with $K_{\text{eff}}^{(0)} \equiv K_{\text{eff}}[W_n(r) \equiv 0]$. This is the result presented in [102] and earlier, within the framework of a different approximate approach, in [129]. In this case the steric factor in equation (31) attains the form

$$f_{\text{dc}}^{(\text{sls})}(\theta_0) = 2\phi_0^2(\theta_0)\sum_{n=0}^{\infty} \frac{\phi_n^2(\theta_0)}{(n+1/2)(n+1)}$$

where the superscript ‘sls’ is a tribute to Shoup, Lipari, and Szabo, who reported this result in [102]. The steric factor $f_{\text{dc}}^{(\text{sls})}(\theta_0)$ is a monotonically increasing function of $\theta_0$, interpolating between $f_{\text{dc}}^{(\text{sls})}(\theta_0 = 0) = 0$ and $f_{\text{dc}}^{(\text{sls})}(\theta_0 = \pi) = 1$ (see, e.g. figure 3 in [131]). These limits can be understood as follows. Since for $n \geq 0$ the Legendre polynomials have defined parity, $P_n(x) = (-1)^nP_n(-x)$, and satisfy $P_n(1) = 1$, it follows that for $\theta_0 \rightarrow \pi$ one has $\phi_n(\pi) = 2\delta_{0,n}$ for $n \geq 0$ (equation (20)). Thus for $\theta_0 \rightarrow \pi$ in the sum in the denominator only the term $n = 0$ survives and therefore $f_{\text{dc}}^{(\text{sls})}(\theta_0 = \pi) = 1$. The limit $\theta_0 \rightarrow 0$ is more involved because $P_n(1) = 1$ and thus $\phi_n(\theta_0 = 0) = 0$ for all $n \geq 0$. However, noting that to first order in $(1 - \cos \theta_0)$ one has $\phi_n(\theta_0 = 0) = (2n + 1)(1 - \cos \theta_0)$ (equation (21)), the steric factor $f_{\text{dc}}^{(\text{sls})}$ behaves as $f_{\text{dc}}^{(\text{sls})}(\theta_0 \rightarrow 0) \propto 1/2\sum_{n=0}^{\infty} \frac{(2n + 1)^2}{(n+1/2)(n+1)}$ and thus vanishes in the limit $\theta_0 \rightarrow 0$ due to the divergence of the series in the denominator. The exact asymptotic behavior in this latter limit was analyzed thoroughly in [102] and [131], and more recently, in [134] with the result that in the limit $\theta_0 \rightarrow 0$ the effective steric factor behaves as $f_{\text{dc}}^{(\text{sls})}(\theta_0 \rightarrow 0) = 3\pi/32$ $\theta_0$. The geometric steric factor $f_g = \sin^2(\theta_0/2)$ behaves as $f_g(\theta_0 \rightarrow 0) = (\theta_0)^2/4$ and hence is much smaller than $f_{\text{dc}}^{(\text{sls})}$. This implies that in the limit $\theta_0 \rightarrow 0$ the first term on the right-hand side of equation (28) becomes the dominant one ($K^* \sim (\theta_0)^2$ while $K_{\text{SD}}f_g(\theta_0) \sim \theta_0$ for $\theta_0 \rightarrow 0$), so that the reaction becomes kinetically controlled. Interestingly, in the case in which precisely one half of the particle is covered by catalyst, i.e. for a so-called Janus particle, the value $f_{\text{dc}}^{(\text{sls})}(\theta_0 = \pi/2) \approx 0.706$ substantially exceeds $1/2$, which is the value of the geometric steric factor for the same coverage.

In the case $W_n \equiv 0$, without the explicit dependence of $g_n$ on $W_n(r)$ being available in closed form for arbitrary $\theta_0$, one cannot state much concerning the behavior of the steric factor in equation (31), except that (based on the same argument as above) for arbitrary potentials $W_n(r)$ it equals 1 for $\theta_0 = \pi$, i.e. $f_{\text{dc}}(\theta_0 = \pi) = 1$ if the whole surface of the particle is catalytic. In the opposite limit of having no catalytic properties, i.e. $\theta_0 \rightarrow 0$, some general statements concerning the form of the coefficients belonging to the leading terms where made recently [134].

As discussed above, in the case that the catalytic patch covers the entire surface of the colloid, i.e. if $\theta_0 = \pi$, one has $f_{\text{dc}}(\theta_0 = \pi) = 1$ for arbitrary $W_n(r)$. In this case one therefore recovers the classic result [126] (see also [135, 136])

$$\frac{1}{K_{\text{eff}}} = \frac{1}{K^*} + \frac{1}{K_{\text{SD}}}, \theta_0 = \pi, \quad W_n(r) \equiv 0.$$  

(34)

If in addition there is no interaction potential $W_n(r)$ one has $K^* = K$ and $R_D = R$. In this case equation (34) reduces to the celebrated relation

$$\frac{1}{K_{\text{eff}}} = \frac{1}{K} + \frac{1}{K_{S}}, \theta_0 = \pi, \quad W_n(r) \equiv 0,$$

(35)

due to Collins and Kimball [122]. The relation in equation (35) can be derived also from microscopic stochastic dynamics which allows one to identify the elementary reaction act constant $K$ through the reaction probability $p$ [137].
In the diffusion-controlled limit corresponding to \( K^* \to \infty \) (and with \( D_A \) fixed, such that the molecular diffusion is the rate-limiting step), the effective reaction constant \( K_{\text{eff}} \) is given by (see equation (28))

\[
K_{\text{eff}}(K^* \to \infty) = K_{SD} f_\theta(\theta_0).
\]

(36)

Combining equations (26) and (36), in the diffusion-controlled limit the factor \( Q \) can be written as

\[
Q(K^* \to \infty) = \frac{n_0 K_{SD} f_\theta(\theta_0)}{2\pi R^2 \phi_\theta(\theta_0)}
\]

(37)

In this case, the coefficients \( a_n \) in equation (27), which enter into the series representation of the number density profile of the reactant (equation (14)), can be written as

\[
a_n(K^* \to \infty) = \frac{R_B e^{iW_B(R)}}{R K_S g'_\theta(R) \phi_\theta(\theta_0)} f_\theta(\theta_0), \quad n \geq 0.
\]

(38)

Finally, for completeness we note that according to equation (27) in the kinetically-controlled limit, in which \( K^* \) is fixed while \( D_A \to \infty \), such that \( K_{\text{eff}} \to K^* \), the coefficients \( a_n \) reduce to

\[
a_n(D_A \to \infty) = \frac{K}{K_S} \frac{1}{R K_S g'_\theta(R) \phi_\theta(\theta_0)}, \quad n \geq 0.
\]

(39)

Since \( K_S = 4\pi D_A R \), in this limit the coefficients \( a_n \) decay with \( D_A \) as \( a_n \sim 1/D_A \) so that \( n_A \) converges to the equilibrium distribution \( n_0(r) \equiv n_0 e^{-iW_B(r)} \) (see equation (14)) if \( D_A \to \infty \). In this extreme limit \( n_A \) does not depend on the angle \( \theta \), and thus equation (11) turns to an exact expression. If the diffusion constant of the \( A \) molecules is finite, (recall that the kinetically-controlled limit should be interpreted as \( K^* < K_{SD} f_\theta(\theta_0) \)), and thus the coefficients \( a_n \neq 0 \) are nonzero, albeit small in magnitude), the chemical reaction enforces an angular dependent, out-of-equilibrium steady state for the distribution of the reactant molecules.

3.3. Steady state distributions of the reaction products

For \( r > R \) the local number density of the reaction products \( B \) obeys the differential equation

\[
0 = \frac{D_B}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial n_B}{\partial r} \right) + \frac{\beta D_B}{r^2} \frac{\partial}{\partial r} \left( r^2 n_B \frac{\partial W_B}{\partial r} \right) + \frac{D_B}{r^2 (\sin \theta)} \frac{\partial}{\partial \theta} \left( \frac{\sin \theta}{\partial \theta} \frac{\partial n_B}{\partial \theta} \right)
\]

(40)

which has the same form as equation (5). Equation (40) is to be solved subject to a sink boundary condition at macroscopic distances from the colloid:

\[
n_B \big|_{r \to \infty} = 0,
\]

(41)

which has to be complemented by the reaction boundary condition across the catalytic patch and the zero current boundary condition across the non-catalytic part of the surface, similar to those for the \( A \) molecules. Within the approximation as used above, these latter two conditions can be combined into the equation

\[
D_B (n_B' + \beta n_B W_B) \big|_{r = R} = -Q (\theta_0 - \theta),
\]

(42)
where we have used the fact that the creation of a \( B \) molecule is tied to the annihilation of an \( A \) molecule so that here the current is opposite to the one on the right hand side of equation (11). (With \( Q > 0 \), the signs in equation (42) correspond, as they should, to molecules of species \( B \) being ‘released’ into the solution.) We seek the stationary solution of equation (40) via the ansatz

\[
n_b(r, \theta) = n_0 e^{-\beta W_B(r)} \sum_{n=0}^{\infty} b_n j_n(r) P_n(\cos \theta),
\]

where \( b_n \) are dimensionless coefficients to be determined from the boundary condition in equation (42). This ansatz solves the stationary equation (40) provided the functions \( j_n(r) \) are those solutions of

\[
\frac{\partial}{\partial r} \left( r \frac{\partial j_n(r)}{\partial r} \right) + \frac{n(n+1)}{r^2} j_n(r) = 0
\]

which vanish for \( r \to \infty \). As for the functions \( g_n(r) \) in equation (15) we choose the normalization \( j_n(r = R) = 1 \). For the interaction potential \( W_B(r) \) we require similar properties as for \( W_A \), i.e. being continuous and bounded, with continuous and bounded first derivative, and vanishing for \( r \to \infty \) (see the previous section). The potential \( W_B(r) \) does not comprise the hard-core repulsion, which is taken into account by the boundary condition in equation (42). Following the same steps as for the case of the reactants and recalling the relation between \( Q \) and \( K_{\text{eff}} \) in equation (26), we obtain the coefficients \( b_n \) in the series representation of \( n_B(r) \):

\[
b_n = -Q \frac{e^{\beta W_B(R)}}{2 D_B n_0} \frac{\phi_n(\theta_0)}{j_n(R)}
\]

\[
= - \frac{K_{\text{eff}}}{4\pi D_B R} \frac{e^{\beta W_B(R)}}{R j_n(R)} \frac{\phi_n(\theta_0)}{\phi_0(\theta_0)}, \quad n \geq 0.
\]

In the diffusion-controlled limit corresponding to \( K^* \to \infty \) the latter equation reduces to

\[
b_n(K^* \to \infty) = -\frac{D_A}{D_B} \frac{R_0}{R} \frac{e^{\beta W_B(R)}}{R j_n(R)} \frac{\phi_n(\theta_0)}{\phi_0(\theta_0)} f_{dc}(\theta_0), \quad n \geq 0.
\]

We note that, via \( Q \) (see equation (22)) in the boundary condition in equation (42), \( n_B(r, \theta) \) depends on the characteristics of the \( A \) particles such as \( n_0, D_A, \) and \( W_A(r) \). On the other hand, \( n_A(r, \theta) \) is independent of the characteristics of the \( B \) particles; this is due to the absence of interactions between \( A \) and \( B \) molecules. In equation (46) \( R_0 \) and \( f_{dc}(\theta_0) \) are the expressions given by equations (17) and (31), respectively. Thus they are determined by \( W_A(r) \) only and are independent of \( W_B(r) \).

In the kinetically-controlled limit, corresponding to \( D_A \to \infty \) with \( K^* \) fixed such that \( K_{\text{eff}} \to K^* \); we have

\[
b_n(D_A \to \infty) = -\frac{K^*}{4\pi D_B R} \frac{e^{\beta W_B(R)}}{R j_n(R)} \frac{\phi_n(\theta_0)}{\phi_0(\theta_0)}, \quad n \geq 0.
\]

In this limit the coefficients \( b_n \) are independent of \( D_A \) and nonzero.

Finally, we note that the distribution of the product molecules \( C \), in the case of the reaction described in equation (2), can be calculated in a similar way. We relegate these straightforward calculations to appendix B.
4. The force exerted on an immobile colloid and the velocity of a force-free colloid

In this section we consider the two contributions to the force exerted on the colloid due to the chemical reaction. They stem (i) from the hydrodynamic flow of the mixture, driven by the inhomogeneous distribution of the components and their interactions with the colloid, and (ii) from the interactions with the reactants, products, and solvent molecules. For brevity, we focus on the $A + CP \rightarrow B + CP$ reaction (equation (1)); the generalization to the case of the catalytically induced dissociation (equation (2)) is straightforward and we will merely list the corresponding results.

4.1. Hydrodynamics of the solution

The conservation of momentum for the mixture requires that the barycentric velocity $\mathbf{u}$ satisfies the Navier–Stokes equations [138]. At steady state and under the assumption that the Reynolds number $\operatorname{Re} = R \rho U_0/\mu$ is very small (which typically is the case for the flows generated by catalytically active colloids [9, 43, 93, 101]), for an incompressible Newtonian fluid of spatially and temporally constant viscosity $\mu$ and mass density $\rho$, subject to the force density $\mathbf{f}(\mathbf{r})$, the Navier–Stokes equations are replaced by the Stokes equations [138]:

$$\nabla \cdot \mathbf{f} = -\mathbf{f} \Rightarrow \mu \mathbf{u} = \nabla P - \mathbf{f},$$

$$\nabla \cdot \mathbf{u} = 0.$$  (48)

In these equations $\mathbf{f}$ denotes the external force density acting on the mixture as a body force (such as, e.g. gravity or the forces due to the interaction of the molecules in the mixture with the colloid) while $\mathbf{f}$ is the Newtonian stress tensor

$$\mathbf{f}_{ij} = -P \delta_{ij} + \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right).$$  (49)

The scalar pressure field $P(\mathbf{r})$, which is equal to 1/3 of the trace of the stress tensor, plays the role of an auxiliary field ensuring that the velocity field $\mathbf{u}$ obeys the incompressibility condition $\nabla \cdot \mathbf{u} = 0$.

Under the assumption that the mass density $\rho$ of the solution is spatially uniform, gravity plays no role here. Thus for the present system the force density $\mathbf{f}$ acting on the solution is solely due to the interactions of the colloid with the molecules in the mixture:

$$\mathbf{f} = -(n_A \nabla \Phi_A + n_B \nabla \Phi_B + n_S \nabla \Phi_S)$$

$$= -\frac{\rho}{m_S} \nabla \Phi_S - (n_A \nabla W_A + n_B \nabla W_B)$$

$$=: -\frac{\rho}{m_S} \nabla \Phi_S + \mathbf{f}.$$  (50)

Here we have used the definition (equation (3)) of the interaction potentials $W_{A,B}$ and the fact that, by definition, $n_S = (\rho - n_A m_A - n_B m_B)/m_S$ (equation (A.1)). Since $\rho$ and $m_S$ are constants, and noting that $\Phi_S$ depends only on $r$, the term $(\rho/m_S)\Phi_S$ can be included in the definition of the

---

7 $P(\mathbf{r})$ is obtained as the solution of the Poisson equation $\nabla^2 P = \nabla \cdot \mathbf{f}$, which follows by taking the divergence of the first equation in equation (48), subject to the boundary condition that $P(r \rightarrow \infty) = P_0$, where $P_0$ is the (spatially constant) bulk value of the pressure. Since no other boundary condition is imposed on $P$, the remaining integration constants are determined, after solving for $\mathbf{u}$, by requiring that $\nabla \cdot \mathbf{u} = 0$ is satisfied.
pressure $P$ (i.e. the isotropic part of the stress tensor). Thus the force exerted by the colloid on the small volume element $\delta V$ of the solution is given by $f \delta V$, with $f = - (n_A \nabla W_A + n_B \nabla W_B)$, and $f$ replaces $\tilde{f}$ in equation (48).

The solution $u(r)$ of equation (48) is subject to appropriate boundary conditions. At the surface of the colloid we assume the usual no-slip boundary condition to hold. Here, it is convenient to consider the general case that the colloid is in motion with velocity $V = V e_z$; the case of an immobile colloid is obtained by setting $V = 0$. In the laboratory (fixed) system of reference, the no-slip boundary condition on the surface of the colloid then takes the form

$$\left. u \right|_{r=R} = V.$$  \hfill (51)

Far away from the colloid the mixture is taken to be at rest, i.e.

$$|u(r \to \infty)| = 0.$$  \hfill (52)

From equations (48), (50)–(52), with the densities $n_A$ and $n_B$ computed according to the steps described in section 3, in principle the hydrodynamic flow $u(r)$ is obtained (in practice may be in a very involved way) as a function of the yet unknown constant velocity $V$ of the colloid. The additional equation needed in order to complete the calculation follows from the condition that the colloid is in steady-state motion, which implies a vanishing net force acting on the colloid. Therefore one has

$$\int_{r=R} \, dS \, \tilde{\Pi} \cdot \epsilon_r + \int_V \, d\mathbf{r} \left(- f \right) + F_{\text{ext}} = 0,$$  \hfill (53)

where the first term is the hydrodynamic force $F_{\text{hyd}}$ acting on the colloid due to the flow of the surrounding solution, and the second term accounts for the force $F_{\text{chem}}$ on the colloid due to the interaction with the molecules in solution. Since the colloid exerts a force $f \, dV$ on the volume element $dV$ of the solution, due to Newton’s third law an opposite force of equal magnitude is exerted by $dV$ on the colloid. The last term $F_{\text{ext}}$ is the sum of all external forces (e.g. an optical trapping) acting on the colloid. The typical set-up is that the external forces are given and the quantity of interest is the velocity of the colloid $V$, which is determined from equation (53).

We are interested in:

(i) the particular case of force free motion, i.e. finding the velocity $V$ if $F_{\text{ext}} = 0$; and

(ii) the external force $F_{\text{ext}}$ needed to immobilize the colloid, so that $V = 0$.

These two quantities are calculated in section 4.3 by using the reciprocal theorem [108, 109] which allows one to by-pass the issue of solving the complex hydrodynamics problem laid out above.

Before proceeding with these analyses, a succinct discussion of each of the terms in equation (53) in terms of their experimental accessibility is in order. Obviously, $F_{\text{ext}}$ is that contribution which is simplest to access as it accounts for external, prescribed forces acting on the colloid. The first and second terms account for contributions which seem to be difficult, if not impossible, to separate from each other, and thus de facto cannot be accessed directly. The first term, $F_{\text{hyd}}$, requires knowledge of the hydrodynamic flow in order to be able to compute the stress tensor $\tilde{\Pi}$. (Here it is important to note that for the system under study the pressure part—including the term $\sim \Phi_S$—of the stress tensor $\tilde{\Pi}$ is isotropic and therefore does not contribute to $F_{\text{hyd}}$.) In principle this can be achieved, although being technically very challenging, by using methods such as particle image velocimetry, as shown in [139] for swimming microorganisms.

The second term, which we consider to be the ‘chemical’ contribution $F_{\text{chem}}$, can be calculated...
if the distributions of the molecular species can be measured (assuming the potentials \( W_{A,R} \) to be known). While one can think of methods such as fluorescence spectroscopy to determine the spatial distribution of chemical species, if they are fluorescent, it is likely that in general it will be very difficult, if not impossible, to determine experimentally the dependence of these distributions on \( r \) and \( \theta \). However, as we show in the following section, the problem can be reduced to that of knowing only their first moment rather than the whole distribution, which may turn out to be a significant step towards rendering \( F_{\text{chem}} \) experimentally accessible.

4.2. Force contribution \( F_{\text{chem}} \) due to the anisotropic distributions of reactants, products, and solvent

Once the steady state spatial distributions of reactants (\( A \)) and products (\( B \)) are known, the force \( F_{\text{chem}} \), they exert on the immobile colloid due to the interaction potentials \( W_{A} \) and \( W_{B} \) can be computed. Since the potential \( \Phi_{S} \) is radially symmetric and the mass density \( \rho \) is uniform due to incompressibility, for a spherical colloid the first term in equation (50) does not contribute to the force \( F_{\text{chem}} = - \int_{V} d^{3}r \mathbf{f} \), where \( V \) denotes the (macroscopic) volume of the reaction bath. Furthermore, because of the axial symmetry of the system, only the \( z \)-component of this force is non-zero so that \( F_{\text{chem}} = F_{\text{chem}}^{z} \). According to equations (50), (14) and (43) this component is given by

\[
F_{\text{chem}}^{z} = -\mathbf{e}_{z} \cdot \int_{V} d^{3}r \mathbf{f} = -\left[ \int_{V} d^{3}r \left( -n_{A} \nabla W_{A} - n_{B} \nabla W_{B} \right) \right] \cdot \mathbf{e}_{z} \\
= 2\pi \int_{0}^{\infty} r^2 dr \int_{0}^{\pi} d\theta \sin \theta \left( n_{A} W'_{A} + n_{B} W'_{B} \right) \cos \theta \\
= \frac{4\pi n_{0}}{3} \left( a_{1} I_{A} + b_{1} I_{B} \right) \\
(54)
\]

where

\[
I_{A} = \int_{R}^{\infty} dr r^2 g_{1}(r) W'_{A}(r) e^{-\beta W_{A}(r)}, \\
I_{B} = \int_{R}^{\infty} dr r^2 j_{1}(r) W'_{B}(r) e^{-\beta W_{B}(r)}, \\
(55)
\]

and \( a_{1} \) and \( b_{1} \) are given, for arbitrary \( K^{*} \), by equation (27) and equation (45), respectively. We note that the above expressions for \( I_{A} \) and \( I_{B} \) are exactly valid, while the expression in equation (54) is approximate, because the factors \( a_{1} \) and \( b_{1} \) are determined by using an approximate, self-consistent approach (see the discussion at the end of section 3.1).

Since \( W_{A} \) and \( W_{B} \) vanish for \( r \to \infty \), in this limit the terms \( \beta W'_{A} \) and \( \beta W'_{B} \) multiplying \( g'_{m} \) in equations (15) and (44) decay more rapidly than the term \( 2/r \) therein and thus represent subdominant contributions. A straightforward perturbation theory analysis then shows (see also appendix D) that for \( r \to \infty \) the leading asymptotic decay of both \( g_{1} \) and \( j_{1} \) is \( 1/r^2 \). Consequently, the integrals in equations (55) are finite. In the limiting case that on the surface of the particle no reaction takes place \( (K^{*} \to 0) \), equation (28) implies that \( K_{\text{eff}} = 0 \) and therefore \( a_{1} = b_{1} = 0 \) [see equations (27) and (45)]. Thus, as expected, at the steady state and in the absence of a chemical reaction one has \( F_{\text{chem}} = 0 \). Obviously this result holds even if the bulk number density of \( B \) molecules is non-zero (i.e. maintained at \( n_{0}^{B} \) by a reservoir, as for species \( A \)). Moreover, for \( K > 0 \), \( W_{A}(r) = W_{B}(r) \), and \( D_{A} = D_{B} \), i.e. if the reaction amounts
to just a re-labeling of the molecules, one has \(a_1 = -b_1\) (see equations (27) and (45)) while \(I_A = I_B\). Therefore, as expected, equation (54) predicts that also in this case one has \(F_{\text{chem}} = 0\).

In the case of diffusion-controlled reactions, i.e. for \(K^* \to \infty\) (see equations (38) and (46)) equation (54) reduces to the simpler form

\[
F_{\text{chem}} = \frac{4\pi n_0 R_D^2}{3 R^2} \Omega^{(AB)}(\Psi(\theta_0), \ K^* \to \infty),
\]

(56)

where

\[
\Omega^{(AB)} = \frac{e^{\omega(R)}}{g'_1(R)} I_A - \frac{D_A}{D_B} \frac{e^{\omega(R)}}{f'_1(R)} I_B
\]

(57)

depends on both interaction potentials and on the ratio of the diffusion coefficients \(D_A/D_B\), but it is independent of the patch size (characterized by \(\theta_0\)). On the other hand, the function \(\Psi(\theta_0)\) absorbs the whole dependence of the force on \(\theta_0\):

\[
\Psi(\theta_0) = \frac{f_\Psi(\theta_0) \phi(\theta_0)}{\phi(\theta_0)} \geq 0,
\]

(58)

where \(f_\Psi(\theta_0)\) is given by equation (31) (and thus it is determined by \(W_A\)), while \(\phi(\theta_0) = 2 \sin^2(\theta_0/2) \geq 0\) and \(\phi(\theta_0) = (3/2) \sin^2(\theta_0) \geq 0\) (equation (20)) are functions of \(\theta_0\) only.

Several general conclusions can be drawn from equation (56), i.e. in the diffusion-controlled limit, upon setting formally \(K^* \to \infty\):

- If the \(A\) and the \(B\) particles have the same interaction potentials with the colloid, i.e. \(W_A(r) \equiv W_B(r)\), so that \(I_A = I_B\) and \(f_1(r) = g_1(r)\) (since \(g_1\) and \(j_1\) fulfill the same differential equation with the same boundary condition to vanish for \(r \to \infty\)), but have different diffusion coefficients, \(D_A \neq D_B\), one has (equations (27), (45) and (54)) \(F_{\text{chem}} \sim (1/D_A)(1 - D_A/D_B)\). Therefore its sign depends on the ratio of the diffusion coefficients. This holds beyond the diffusion-controlled limit \(K^* \to \infty\) (equation (54)).

- For a completely catalytic colloid \((\theta_0 = \pi)\) or a chemically inert one \((\theta_0 = 0)\) one has \(\Psi(\theta_0) = 0\). For \(\theta_0 = \pi\), \(\phi(\pi) = 2\) is nonzero, while \(\phi(\pi) = 0\) and the effective steric factor attains the value \(f_\Psi(\pi) = 1\) (see the discussion following equation (33)). For \(\theta_0 = 0\) this is the case because the ratio \(\phi(0)/\phi(0) = 3\) is finite, while \(f_\Psi(0)\) is expected to vanish (see the discussion following equation (33)). Therefore, as expected, in these cases there is no force \(F_{\text{chem}}\) acting on the particle because the system exhibits full radial symmetry. We remark, however, that our model is a mean-field one, so that one can not rule out the possibility that there will be a non-zero force due to fluctuations in spatial distributions of the reactants and products (see, e.g. the situations discussed in [103, 140]).

- Since \(\Psi(\theta_0)\) is continuous and \(\Psi(0) = \Psi(\pi) = 0\), there exists a catalyst coverage characterized by \(0 < \tilde{\theta}_0 < \pi\) for which \(|F_{\text{chem}}|\) is maximal; \(\tilde{\theta}_0\) is a functional of \(W_A(r)\) and \(W_B(r)\).

- \(F_{\text{chem}}\) can be positive or negative, or equal to zero, depending on the relations between \(W_A(r)\) and \(W_B(r)\) and those between the diffusion coefficients. But the expression in equation (57) is too complex to allow one to obtain analytically exact criteria for certain properties of \(F_{\text{chem}}\).

In the opposite limit, i.e. in the kinetically-controlled regime \((D_A \to \infty, K_{\text{eff}} \to K^*\) fixed), one has (equations (39), (47), (54), (57), (9) and (30))
\[
F_{\text{chem}} = \frac{n_0 K^* \cos^2(\theta_0/2)}{R^2} \left( I_A e^{\beta W_A(R)} - I_B e^{\beta W_B(R)} \right) \\
= \pi n_0 \alpha W_0 e^{-\beta W_A(R)} \Omega_{AB}^C (\sin \theta_0)^2,
\]

which shows that the force \( F_{\text{chem}} \) vanishes in perfectly stirred systems, in which both \( D_A \) and \( D_B \) tend to infinity. For \( D_{A,B} \) very large but finite, it is obvious that all the above bullet points apply to this case, too. Moreover, in this case the strength of the force attains its maximum at \( \theta_0 = \pi/2 \), i.e. for a symmetric Janus colloid.

Lastly, we note that the result in equation (54) can be straightforwardly generalized in order to cover the dissociation reaction described in equation (2). For this case we find that the force \( F_{\text{chem}} \) exerted on the colloid by the ‘frozen’ spatial distributions of the \( A, B, C \), and \( S \) molecules due to the interaction potentials \( \Phi_A, \Phi_B, \Phi_C, \) and \( \Phi_S \) (compare equation (50)), respectively, is given by (compare equation (54))

\[
F_{\text{chem}} = - \left[ \int_{\phi} d^4 r \left( -n_A \nabla W_A - n_B \nabla W_B - n_C \nabla W_C \right) \right] \cdot \hat{e}_z
\]

\[
= \frac{4 \pi n_0}{3} (a I_A + b I_B + \gamma I_C),
\]

where, for arbitrary \( K^* \), \( a, b, \) and \( \gamma \) are given by the corresponding equations (27), (45) and (B.4), respectively, the expressions \( I_A \) and \( I_B \) are defined in equation (55), and

\[
I_C = \int_{R} r^2 h(r) W_C'(r) e^{-\beta W_C(r)}.
\]

(Similarly as the expressions for \( I_A \) and \( I_B \), the expression \( I_C \) for the force integral is exact, too.)

Accordingly, using equations (38), (46) and (B.5) one finds for the diffusion-controlled regime (compare equation (56))

\[
F_{\text{chem}}(K^* \to \infty) = \frac{4 \pi n_0 R D}{3 R^2} \Omega_{ABC} \Psi(\theta_0).
\]

\( \Omega_{ABC} \) depends on the relative interaction potentials \( W_A, W_B, \) and \( W_C \), as well as on the ratios \( D_A/D_B \) and \( D_B/D_C \) of the diffusion coefficients:

\[
\Omega_{ABC} = \frac{e^{\beta W_A(R)}}{g_1'(R)} I_A - \frac{D_A}{D_B} \frac{e^{\beta W_B(R)}}{f_1'(R)} I_B - \frac{D_B}{D_C} \frac{e^{\beta W_C(R)}}{h_1'(R)} I_C.
\]

But \( \Omega_{ABC} \) is independent of the catalytic patch size characterized by \( \theta_0 \). As before, the whole dependence on \( \theta_0 \) is captured by the factor \( \Psi(\theta_0) \) defined in equation (58).

For the kinetically-controlled regime one has (compare equation (59))

\[
F_{\text{chem}} = \pi n_0 \alpha W_0 \frac{e^{-\beta W_A(R)}}{D_A} \Omega_{ABC}^C (\sin \theta_0)^2.
\]

The force \( F_{\text{chem}} \) vanishes in perfectly stirred systems, in which \( D_A, D_B, \) and \( D_C \) tend to infinity.
4.3. The velocity of a force-free catalytically-active colloid and the force needed to immobilize it

At steady state and upon neglecting the thermal fluctuations giving rise to rotational diffusion of the symmetry axis in \( z \) direction, the results obtained so far can be straightforwardly employed to determine the velocity \( \mathbf{V} = \mathbf{V}_e \) of an active colloid in ‘force free’ (i.e., \( \mathbf{F}_{\text{ext}} = 0 \)) motion, or the external force \( \mathbf{F}_{\text{ext}} = \mathbf{F}_{\text{ext}}^e \) needed to immobilize the active colloid (i.e., \( \mathbf{V} = 0 \)).

The calculation is based on employing the generalized reciprocal theorem due to Teubner (see appendix C) \cite{93, 100, 108, 109}. This states that for two incompressible Newtonian flows characterized by \( \{ \mu, \mathbf{u}, \hat{\Pi} \} \) and \( \{ \mu', \mathbf{u}', \hat{\Pi}' \} \), respectively, and solving the Stokes equations (equation (48)) for force densities \( \mathbf{f} \) and \( \mathbf{f}' \), respectively, within the domain \( \mathcal{D} \) exterior to a closed surface \( \partial \mathcal{D} \), whereby \( \hat{\Pi}, \mathbf{u}, \) and \( \mathbf{f} \), as well as the primed ones, vanish sufficiently fast with increasing distance from \( \partial \mathcal{D} \), the following relation holds \cite{109}:

\[
\mu' \left[ \int_{\partial \mathcal{D}} \mathbf{u}' \cdot \hat{\Pi}' \cdot d\mathbf{s} - \int_{\mathcal{D}} \mathbf{u}' \cdot \mathbf{f}' \, d\mathbf{r} \right] = \mu \left[ \int_{\partial \mathcal{D}} \mathbf{u} \cdot \hat{\Pi} \cdot d\mathbf{s} - \int_{\mathcal{D}} \mathbf{f} \cdot d\mathbf{r} \right].
\]

(65)

Here the orientation of the surface element \( d\mathbf{s} := d\mathbf{s}_e \) is the one given by the inner normal (i.e. pointing into the fluid domain \( \mathcal{D} \)).

For the unprimed system we choose the fluid motion as the one corresponding to the self-propelled colloid moving with velocity \( \mathbf{V} = \mathbf{V}_e \) (in this case \( \partial \mathcal{D} \) is the surface \( \mathcal{R} \) of the sphere and the fluid domain \( \mathcal{D} \) is the volume \( \mathcal{V} \) of the solution):

\[
\nabla \cdot \hat{\Pi} = -\mathbf{f} := -f \mathbf{e}_r, \nabla \cdot \mathbf{u} = 0,
\]

\[
\mathbf{u}(r = R) = \mathbf{V}_e, \quad \mathbf{u}(r \to \infty) = 0,
\]

(66)

where in the first equation we have used the fact that \( \mathbf{f} \) has only a radial component \( f := \mathbf{f} \cdot \mathbf{e}_r \) (due to \( \mathbf{W}_{A,B} \) being radially symmetric, see equation (50)).

For the primed system we choose the one corresponding to the motion of the fluid (of the same viscosity, i.e. \( \mu' = \mu \)) due to a sphere of radius \( R \) translating along the \( z \)-direction with uniform velocity \( \mathbf{U}_0 = \mathbf{U}_0 \mathbf{e}_z \):

\[
\nabla \cdot \hat{\Pi}' = 0, \nabla \cdot \mathbf{u}' = 0,
\]

\[
\mathbf{u}'(r = R) = \mathbf{U}_0 \mathbf{e}_z, \quad \mathbf{u}'(r \to \infty) = 0.
\]

(67)

For the latter system the solution is known and the axially symmetric velocity field \( \mathbf{u}' \) is given in spherical coordinates by (see, e.g. chapter 4 in \cite{138})

\[
\mathbf{u}' = \frac{\mathbf{U}_0}{2} \left[ 3 \left( \frac{R}{r} \right) - \left( \frac{R}{r} \right)^3 \right] \cos \theta := \mathbf{U}_0 \xi(r) \cos \theta,
\]

\[
\mathbf{u}'_e = -\frac{\mathbf{U}_0}{4} \left[ 3 \left( \frac{R}{r} \right) + \left( \frac{R}{r} \right)^3 \right] \sin \theta.
\]

(68)

By using equations (66) and (67), and noting that in the latter case \( \mathbf{f}' \equiv 0 \) while \( \mathbf{U}_0 \) and \( \mathbf{V} \) are constants with respect to the integration over the spherical surfaces, equation (65) leads to

\[
\mathbf{U}_0 \cdot \int_{\mathcal{F} = \mathcal{R}} \hat{\Pi}' \cdot \mathbf{e}_r \, d\mathcal{S} - \int_{\mathcal{V}} \mathbf{u}' \cdot \mathbf{f} \, d\mathbf{r} = \mathbf{V} \cdot \int_{\mathcal{F} = \mathcal{R}} \hat{\Pi}' \cdot d\mathbf{s}.
\]

(69)

The last integral is the drag force acting on the translating sphere and it is given by the well known Stokes formula (see, e.g. chapter 4 in \cite{138}). \( \int_{\mathcal{F} = \mathcal{R}} \hat{\Pi}' \cdot d\mathbf{s} = -6\pi \mu \mathbf{R} \mathbf{U}_0 \). By noting that
the surface integral on the left hand side of equation (69) is the contribution $F_{\text{hyd}}$ of the force acting on the colloid, and by using equation (53) to eliminate it in favor of the other two force contributions, we arrive at

$$U_0 \cdot [-F_{\text{ext}} + 6\pi \mu R V] = \int_{V} d^3r (u' - U_0) \cdot f. \tag{70}$$

The two cases of interest are immediately obtained from the general result in equation (70) as follows.

(i) Velocity of the force free colloid.

With $F_{\text{ext}} = 0$, and by noting that $\cos \theta = e_z \cdot e_r$, equation (70) renders

$$V = \frac{1}{6\pi \mu R} \int_{V} d^3r [\xi(r) - 1] f \cos \theta
= \frac{1}{6\pi \mu R} \int_{V} d^3r \left[\frac{3}{2} \left(\frac{R}{r}\right)^3 - \frac{1}{2} \left(\frac{R}{r}\right)^3 \right] f \cos \theta. \tag{71}$$

(We recall that $f = f \cdot e_r$, with $f$ given by equation (50).)

As the next step, using the equality in the first line in equation (54), we express the self-propulsion velocity $V$ in terms of the coefficients with index $n = 1$ in the expansions of the densities of the reactants and products. For the simplest type of reaction $A + CP \to B + CP$, one has

$$V = \frac{2n_0}{9\mu R} (a_1J_A + b_1J_B), \tag{72}$$

where

$$J_A = \int_{R}^{\infty} dr r^2 g(r) W_A'(r) \left(1 + \frac{1}{2} \left(\frac{R}{r}\right)^3 - \frac{3}{2} \frac{R}{r} \right) e^{-\beta \omega_A(r)} \tag{73}$$

and

$$J_B = \int_{R}^{\infty} dr r^2 g(r) W_B'(r) \left(1 + \frac{1}{2} \left(\frac{R}{r}\right)^3 - \frac{3}{2} \frac{R}{r} \right) e^{-\beta \omega_B(r)}. \tag{74}$$

Similarly as the expressions $I_A$ and $I_B$ for the force integrals, the expressions $J_A$ and $J_B$ for the velocity integrals are exact, too.

In turn, for a more general catalytically-induced dissociation in equation (2) we obtain

$$V = \frac{2n_0}{9\mu R} (a_1J_A + b_1J_B + \gamma \lambda), \tag{75}$$

where $\gamma$ is defined in equation (B.4) and

$$J_C = \int_{R}^{\infty} dr r^2 g(r) W_C'(r) \left(1 + \frac{1}{2} \left(\frac{R}{r}\right)^3 - \frac{3}{2} \frac{R}{r} \right) e^{-\beta \omega_C(r)}. \tag{76}$$

(ii) Stall force $F_{\text{ext}}$ needed to immobilize a colloid.

With $V = 0$ and $\cos \theta = e_z \cdot e_r$, equation (70) yields

$$F_{\text{ext}} = - \int_{V} d^3r [\xi(r) - 1] f \cos \theta. \tag{77}$$
The stall force is proportional to the velocity $V_{\text{free}}$ (equation (71)) of a force-free colloid,

$$F_{\text{ext}} = -6\pi \mu R V_{\text{free}},$$  \hspace{1cm} (78)$$

and has the same form as the Stokes formula. This result follows directly from equation (70). Therefore it is very general, in the sense that this result does not depend on the details of the chemical activity but only on the assumptions of a spherical shape, steady state motion, and (negligibly) small Re and Pe numbers.

Therefore, by using equations (72) and (75) $F_{\text{ext}}$ can be expressed explicitly as

$$F_{\text{ext}} = -\frac{4\pi \mu_0}{3}(a_iJ_A + b_iJ_B), \hspace{1cm} A \rightarrow \text{CP}$$

and as

$$F_{\text{ext}} = -\frac{4\pi \mu_0}{3}(a_iJ_A + b_iJ_B + \gamma_iJ_C), \hspace{1cm} A \rightarrow \text{CP} \rightarrow \text{C} + \text{CP},$$

respectively.

5. Triangular-well potentials as a case study

We illustrate the general results derived in the previous section by choosing a particular form of the interaction potential between the colloid and the various molecular species involved in the reaction. This allows us to obtain sufficiently simple explicit expressions for the force contribution $F_{\text{chem}}$ (equation (60)), the stall force $F_{\text{ext}}$ (equation (78)), or, equivalently, the velocity $V$ (equation (71)) of a force-free colloid, such that their dependences on the strength of the interactions, catalytic coverage, chemical rates, diffusion coefficients of the reactants and products, and radius of the colloid can be determined and discussed. This choice is provided by the so-called triangular-well potentials (depicted in figure 2) which, despite their simplicity, capture well the thermodynamic properties of fluids with Lennard-Jones pair interactions, provided the defining parameters of the triangular-well potentials are tuned suitably (see, e.g. [110–112] for a detailed discussion of this issue). For this choice of the potential one can derive explicit formulae for the chemical and the stall force, which allows one to highlight several counter-intuitive effects concerning diffusiophoretic self-propulsion.

We stipulate that the potential $W_j(r)$ for the interactions of the colloid with the $j$th species ($j = A, B, C$) is a piece-wise continuous function defined as follows (see figure 2):

$$W_j(R \leq r \leq R + \lambda_j) \equiv W^j_\Lambda(r) = -\xi_{ij}^j r + (W_j(R) + \xi_{ij}^j R),$$

where

$$\xi_{ij}^j = \frac{W_j(R) - W_j(R + \lambda_j)}{\lambda_j} = \frac{\Delta \xi_{ij}}{\beta \lambda_j}$$

with

$$\Delta \xi_{ij} \equiv \varepsilon_{ij}^\Lambda - \varepsilon_{ij}^\Lambda = \beta W_j(R) - \beta W_j(R + \lambda_j)$$

in the inner region $r \in (R, R + \lambda_j)$;

$$W_j(R + \lambda_j \leq r \leq R + \Lambda_j) \equiv W^j_{\Lambda}(r) = \xi_{ij}^j r - \xi_{ij}^j (R + \Lambda_j),$$
where

\[ \xi_2 = -\frac{\epsilon_m^j}{\beta(\Lambda_j - \lambda_j)}, \quad (85) \]

in the intermediate region \( r \in (R + \lambda_j, R + \Lambda_j) \). In the outer region \( r \in (R + \Lambda_j, \infty) \) the potential vanishes:

\[ W_j(r \geq R + \Lambda_j) \equiv W_j^*(r) \equiv 0. \quad (86) \]

The parameters (the value at the wall, the depth, and the location of the well) defining the interactions of the colloid with the \( j \)th species are, in general, different. In the following we shall focus the discussion of the results on the situation depicted in figure 2, i.e. \( \Delta \epsilon_j > 0 \) and \( \epsilon_m^j \leq 0 \). (Nonetheless, the derivation of the results is carried out for both signs of these parameters.)

Furthermore, we introduce the dimensionless parameters \( q_j = \lambda_j/R, Q_j = \Lambda_j/R \), and \( z_j = Q_j/q_j \geq 1 \). The derivation of the radial functions \( g_a(r) \) (equation (15)) for arbitrary values of the parameters \( q_A \) and \( Q_A, \epsilon_m^A \) and \( \epsilon_m^A \) is detailed in appendix D. (The corresponding results for the other species follow, as in section 3, by simply switching label \( A \) with \( B \) or \( C \).) Based on these functions, in appendix D we also derive the general expressions for the integrals \( I_j \) (equation (55)) and \( J_j \) (equations (73), (74) and (76)) for \( j = A, B, C \). Here we restrict the discussion to the physically meaningful limit \( \lambda_j/R \ll 1 \) (at fixed \( z_j \geq 1 \)) and retain only the leading order term. For colloids of radii \( R \geq 1 \mu m \) and typical surface interactions, the parameter \( \lambda_j/R \) is expected to be of the order of \( 10^{-2} \) or smaller. Thus the corrections \( O(\lambda_j/R) \) to the leading order term (which are included in appendix D) are expected to be negligibly small.

5.1. The contribution \( F_{chem} \) due to the direct interactions of the colloid with the molecular species

In leading order in \( \lambda_j/R \), the force integrals (equation (55)) are given by

\[ I_j = -\frac{(1 - e^{-z_j})}{\beta} R^2. \quad (87) \]
This shows that, somewhat surprisingly, the leading order value of $I_j$ is controlled only by the value of the potential at the wall and is independent of the depth $\varepsilon_m^j$ of the well. The leading order value of $I_j$ is negative for $\varepsilon_w^j > 0$ (repulsion from the wall) and positive for $\varepsilon_w^j < 0$ (attraction to the wall). The corrections depend on $\varepsilon_m^j$ and may be positive or negative hinging on the relation between $\varepsilon_m^j$ and $\varepsilon_w^j$ (see equation (D.22) in appendix D).

In this limit the Debye radius (equation (17)) is simply given by $R_D = R$ (the correction terms are given by equation (D.2) in appendix D), the steric factor $f_{dc}(\theta_0)$ (equation (31)) turns into $f_{dc}(\theta_0) = f_{dc}^{\text{ids}}(\theta_0)$ (equation (33)), and the derivative of the first radial function at the wall is

$$g'(R) = \frac{-2e^{\varepsilon_w^A}}{R}. \quad (88)$$

Consequently, we find (equations (28)–(30)) that in this limit the coefficient $a_1$ (equation (27)) is

$$a_1 = -\frac{3}{8} \left( \frac{\kappa e^{-\varepsilon_w^A} R}{\sin^2(\theta_0/2) + D_h f_{dc}^{\text{ids}}(\theta_0)} \right) \sin^2(\theta_0) f_{dc}^{\text{ids}}(\theta_0); \quad (89)$$

therefore, the contribution of the A molecules to the force $F_{\text{chem}}$ (equation (54)) is given by

$$F_{\text{chem}}^A = \frac{\pi \eta_0}{2} \left( \frac{\kappa e^{-\varepsilon_w^A}(1 - e^{-\varepsilon_w^A}) R^3}{\sin^2(\theta_0/2) + D_h f_{dc}^{\text{ids}}(\theta_0)} \right) \sin^2(\theta_0) f_{dc}^{\text{ids}}(\theta_0). \quad (90)$$

In this limit, the sign of $F_{\text{chem}}^A$ is determined fully by the sign of $\varepsilon_w^A$: for $\varepsilon_w^A > 0$, i.e. if the A molecules are repelled from the surface of the colloid, $F_{\text{chem}}^A$ is positive. This is a simple consequence of the fact that, due to the reaction, the A molecules are depleted in the region $z > 0$, as compared to the region at the other side of the catalytic patch, which effectively pushes the colloid into the positive $z$-direction. We further remark that $F_{\text{chem}}^A$ is a non-monotonic function of $\varepsilon_w^A$ and vanishes if either $\varepsilon_w^A \rightarrow 0$ or $\varepsilon_w^A \rightarrow \infty$. The latter can be understood by noting that an infinitely strong repulsion prevents the A molecules from approaching the catalytic patch and hence completely suppresses the reaction, which renders a radially symmetric distribution.

We proceed with the calculation of the coefficients $b_1$ and $\gamma_1$ defined in equations (45) and (B.4). Since the derivatives of the radial functions $j_1(r)$ and $h_1(r)$, defined by equations (44) and (B.3), have the same form as $g'(R)$ but with $\varepsilon_w^A$ replaced by $\varepsilon_w^B$ or $\varepsilon_w^C$, in leading order in $\lambda_j R$ the coefficients $b_1$ and $\gamma_1$ are given by

$$b_1 = \frac{3D_h}{8D_h} \left( \frac{\kappa e^{-\varepsilon_w^B} R}{\sin^2(\theta_0/2) + D_h f_{dc}^{\text{ids}}(\theta_0)} \right) \sin^2(\theta_0) f_{dc}^{\text{ids}}(\theta_0), \quad (91)$$

and

$$\gamma_1 = \frac{3D_h}{8D_c} \left( \frac{\kappa e^{-\varepsilon_w^C} R}{\sin^2(\theta_0/2) + D_h f_{dc}^{\text{ids}}(\theta_0)} \right) \sin^2(\theta_0) f_{dc}^{\text{ids}}(\theta_0). \quad (92)$$

Consequently, we arrive at the following explicit expressions for the force $F_{\text{chem}}$.
• the case $A + CP \rightarrow B + CP$:

$$F_{\text{chem}} = \frac{\pi n_0 R^2 D_A}{2\beta} \frac{\kappa e^{-\epsilon^*_w}}{(\kappa e^{-\epsilon^*_w} R \sin^2(\theta_B/2) + D_A f_{dc}^{(sls)}(\theta_0))} \times \left(1 - \frac{1 - e^{-\epsilon^*_w}}{D_B} \right) \sin^2(\theta_0) f_{dc}^{(sls)}(\theta_0); \quad (93)$$

• the case $A + CP \rightarrow B + C + CP$ (dissociation reaction):

$$F_{\text{chem}} = \frac{\pi n_0 R^2 D_A}{2\beta} \frac{\kappa e^{-\epsilon^*_w}}{(\kappa e^{-\epsilon^*_w} R \sin^2(\theta_B/2) + D_A f_{dc}^{(sls)}(\theta_0))} \times \left(1 - \frac{1 - e^{-\epsilon^*_w}}{D_B} \right) - \left(1 - \frac{1 - e^{-\epsilon^*_w}}{D_C} \right) \sin^2(\theta_0) f_{dc}^{(sls)}(\theta_0). \quad (94)$$

If the values $\epsilon^*_w$ are equal to each other, i.e. $\epsilon^*_w = \epsilon^*_w = \epsilon^*_w$, equations (93) and (94) take the simple forms $(A + CP \rightarrow B + CP)$

$$F_{\text{chem}} = \frac{\pi n_0 R^2 D_A}{2\beta} \frac{\kappa e^{-\epsilon^*_w}}{(\kappa e^{-\epsilon^*_w} R \sin^2(\theta_B/2) + D_A f_{dc}^{(sls)}(\theta_0))} \times \left(1 - \frac{1}{D_B} \right) \sin^2(\theta_0) f_{dc}^{(sls)}(\theta_0) \quad (95)$$

and $(A + CP \rightarrow B + C + CP)$

$$F_{\text{chem}} = \frac{\pi n_0 R^2 D_A}{2\beta} \frac{\kappa e^{-\epsilon^*_w}}{(\kappa e^{-\epsilon^*_w} R \sin^2(\theta_B/2) + D_A f_{dc}^{(sls)}(\theta_0))} \times \left(1 - \frac{1}{D_B} \right) - \left(1 - \frac{1}{D_C} \right) \sin^2(\theta_0) f_{dc}^{(sls)}(\theta_0), \quad (96)$$

respectively. Thus, in this case the sign of $F_{\text{chem}}$ is determined by the relation between the diffusion coefficients of the reactive species.

Focusing here on the case of the reaction $A + CP \rightarrow B + CP$, we discuss the limiting behavior of the force $F_{\text{chem}}$ in equation (93), rendering explicit results for several general conclusions presented above in section 4.2. To this end, we first consider the so-called diffusion-limited case and assume that the parameters of the model obey the following inequality:

$$\kappa e^{-\epsilon^*_w} R \sin^2(\theta_0/2) \gg D_A f_{dc}^{(sls)}(\theta_0). \quad (97)$$

(We remark that, in contrast to the case discussed by Collins and Kimball, (equation (35)), here the lhs of the inequality depends also on $\epsilon^*_w$ and both sides depend on $\theta_0$. Therefore, this limit has to be taken with appropriate caution, if one intends to study the dependence of $F_{\text{chem}}$ on $\theta_0$ in the limit $\theta_0 \rightarrow 0$.) Since $\sin^2(\theta_0/2) \sim \theta_0^2$, while $f_{dc}^{(sls)}(\theta_0) \sim \theta_0$, for fixed $\kappa$, $R$, $D_A$, and $\epsilon^*_w$, which obey the inequality in equation (97) for moderate $\theta_0$, the sign of the inequality changes for sufficiently small values of $\theta_0$. In other words, as we have already noted in the text after equation (33), for $\theta_0 \rightarrow 0$ there is always the kinetically-controlled regime, but not the
diffusion-controlled one. Similarly, the dependence of $F_{\text{chem}}$ on $\varepsilon_w^A$ (as well as the one of $F_{\text{ext}}$ or, equivalently, $V$, which will be discussed below) obtained for this regime cannot be extrapolated to arbitrarily large values of $\varepsilon_w^A$. The reason for this is that the effective reduction of the reactivity due to an increase of the repulsion at the wall (and hence, on the catalytic patch) ultimately causes a reversal of the inequality in equation (97).

In the diffusion-controlled limit equation (93) attains the form

$$F_{\text{chem}} = \frac{2\pi m_0 R^2}{\beta} \left(1 - e^{-\varepsilon^A} - \frac{D_A}{D_B}(1 - e^{-\varepsilon^B})\right) \times \cos^2(\theta_0/2) \int_{\text{dc}}^{\text{dc}}(\theta_0).$$

(98)

In this regime, the force is proportional to $R^2$ (i.e. the area of the colloid) and attains its maximal value for $\theta_0$ close to $\pi/2$ (but not exactly equal to it, see the discussion in section 4.2). The sign of the force depends on the diffusion coefficients of both species and on the amplitudes of their interaction potentials with the wall. For

$$\frac{(1 - e^{-\varepsilon^A})}{D_A} \geq \frac{(1 - e^{-\varepsilon^B})}{D_B}$$

(99)

the force $F_{\text{chem}}$ is positive, while it is negative if the inequality is reversed.

In the limit of the kinetic control, if $D_A$ is sufficiently large so that the inequality in equation (97) is reversed, one has

$$F_{\text{chem}} = -\frac{\pi m_0 R^3}{2|D_B|} e^{-\varepsilon^B}(1 - e^{-\varepsilon^B}) \sin^2(\theta_0).$$

(100)

In this regime the force is proportional to the $R^3$ (i.e. volume of the colloid), attains the maximal value for $\theta_0 \equiv \pi/2$, i.e. in the case of Janus particles with the catalytic patch occupying exactly one half of the surface), and its sign is determined by the sign of $\varepsilon_w^B$. For positive values of $\varepsilon_w^B$, i.e. if the products B are repelled from the surface of the colloid, the force $F_{\text{chem}}$ is negative, and is positive in the case of negative values of $\varepsilon_w^B$. In the limit $D_B \to \infty$ the force vanishes $\sim 1/D_B$.

5.2. Stall force $F_{\text{ext}}$ and self-propulsion velocity $V$ of a force-free colloid

Next we turn to the analysis of the stall force $F_{\text{ext}}$ (equations (79) and (80)) and, equivalently (see equation (78)), of the self-propulsion velocity $V$ of a force-free colloid. For the triangular well potentials, the exact expressions for the integrals $J_j$ (equations (73), (74) and (76)) entering the definition of $F_{\text{ext}}$ and $V$ are presented in appendix D. Analogous to the previous section, here we focus on the leading order term in $\lambda_j/\lambda$, which is given by

$$J_j = \frac{\lambda_j^2}{\beta},$$

(101)

with

$$J_j = -\frac{3e^{-\varepsilon^j}}{2\Delta^2} (e^{\Delta^j}(1 + (\Delta^j - 1)^2) - 2)
+ \frac{3}{2(\varepsilon_m^j)(z_j - 1)^2} e^{-\varepsilon_m^j}(1 + z_j e^{-\varepsilon_m^j} - z_j)^2)
+ (\varepsilon_m^j - z_j + 1)^2 e^{-\varepsilon_m^j} - (1 + z_j e^{-\varepsilon_m^j} - z_j)^2).$$

(102)
We note that, in contrast to $I_j$, $J_j$ depends on the depth $\varepsilon_m$ of the potential well even in leading order. Mathematically, this is a consequence of the additional factor $(1 + (R/r)^3/2 - 3R/(2r))$ in the integrands in equations (73), (74) and (76). Consequently, the dependence of $J_j$ on the parameters characterizing the interaction potentials (equations (101) and (102)) is more complex.

In figure 3 we show $J_j$ (equation (102)) as a function of $\varepsilon_w$ for several values of the depth of the well. We observe that even for the smallest value of $\varepsilon_m$ (here, $\varepsilon_m = -0.1$), a significant repulsion at the wall ($\varepsilon_w \approx 0.6$) is needed in order to have $J_j$ becoming negative. This is in contrast to the behavior exhibited by $I_j$, which is negative as soon as $\varepsilon_w$ is negative. For a slightly deeper well ($\varepsilon_m = -0.22$) a much stronger repulsion at the wall ($\varepsilon_w \approx 2$) is required for turning $J_j$ negative. Furthermore, for $\varepsilon_m = -0.5$, $J_j$ remains positive for $\varepsilon_w$ as large as $\varepsilon_w \approx 7$. This leads to the conclusion that, while the sign of $I_j$ is dominated by the value of the interaction potential at the wall, the sign of $J_j$ depends strongly on the depth of the well. Thus, for sufficiently small values of $\varepsilon_w$, one can observe an intriguing behavior in that the contributions $F_{j,\text{chem}}$ and $F_{j,\text{ext}}$, respectively, of the molecular species $j$ to the chemical and stall force, respectively, have the same direction. Due to equation (78) this implies that the self-propulsion velocity $V_j$ and $F_{j,\text{chem}}$ have opposite signs. For small values of $\varepsilon_m$ and $|\varepsilon'_m|$, the Taylor series in powers of $\varepsilon'_m$ and $\varepsilon'_w$ of the right-hand-side of equation (102) can be truncated at first order. In this case, one obtains

$$J_j \approx -\frac{z_j(z_j + 1)}{2} \varepsilon'_w - \frac{1}{2} \varepsilon'_m,$$

which, in the case of sufficiently small interaction parameters $\varepsilon'_m$ and $|\varepsilon'_m|$, provides a simple criterion for the sign of $J_j$, and hence of $F_{j,\text{ext}}$ and $V_j$.

Furthermore, equations (54), (60), (72), (75), (79) and (80) imply that the contribution to $F_{j,\text{ext}}$ (or, equivalently, to $V_j$) due to the interactions with the molecular species $j$ is related to $F_{j,\text{chem}}$ as

$$F_{j,\text{ext}} = \left(\frac{\lambda_j}{R}\right)^2 \frac{J_j}{(1 - e^{-\varepsilon'_w})} F_{j,\text{chem}}$$

Figure 3. Dimensionless factor $J_j$ (equation (102)) in the integral $J_j$ (equation (101)) as a function of $\varepsilon'_w$ for $z_j = \Lambda_j / \lambda_j = 2$ (see figure 2) and $\varepsilon'_w = -0.1$ (solid line), $\varepsilon'_w = -0.22$ (dotted line), and $\varepsilon'_w = -0.5$ (dashed line).
and equivalently,

\[
V_j = -\frac{1}{6\pi \mu R} \left( \frac{\lambda_j}{R} \right)^2 \frac{J_j}{(1 - e^{-\epsilon_j})} F_j^\text{chem}.
\]  

(105)

Equations (104) and (105) lead to various conclusions. First, they show that \( F_j^\text{ext} \) and \( V_j \) are, by a factor \((\lambda_j R)^2\), much smaller than the force contribution \( F_j^\text{chem} \). Second, the dependence of \( F_j^\text{ext} \) (and thus also that of \( V_j \)) on \( \theta_0, \kappa, \) and \( D_j \) comes about only via \( F_j^\text{chem} \). The factor \( J_j/(1 - \exp(-\epsilon_j)) \) implies that only for \( \epsilon_j \) sufficiently large (ensuring that \( J_j > 0 \)) the stall force contribution \( F_j^\text{ext} \) and the velocity contribution \( V_j \) have signs which are opposite and equal, respectively, to \( F_j^\text{chem} \), which one might expect \textit{a priori} on intuitive grounds. These properties are, as explained above, due to the fact that for not too large \( \epsilon_j \) the integrals \( J_j \), which determine \( F_j^\text{ext} \) and \( V_j \), are dominated by the depth of the well, while the integrals \( I_j \), which determine \( F_j^\text{chem} \), are always dominated by \( \epsilon_j \).

The overall dependence of \( V_j \) (or, equivalently, of the contribution \( F_j^\text{ext} \) to the stall force) on \( \epsilon_A \) and \( \epsilon_m \) requires further analysis because, as explained earlier, upon a gradual increase of \( \epsilon_A \) the system, which is in the diffusion-limited regime for small values of this parameter, eventually crosses over into the kinetic control regime. We illustrate this behavior for \( j = A \). The general dependence on \( \kappa \) and \( D_A \) is given by

\[
V_A = -V_0 \left( \frac{\sin^2(\theta_0/2)}{J_A^\text{chem}(\theta_0)} + \frac{D_A}{\kappa R} e^{-\epsilon_A} \right)^{-1} J_A \sin^2(\theta_0), \quad V_0 = \frac{n_0 \lambda_A^2}{12\beta \mu R}.
\]  

(106)

\( V_0 \) is independent of \( \epsilon_A \) and \( \epsilon_m \) while the ratio \( D_A/(\kappa R) \) can be estimated from available experimental data. In particular, for the experimental situation studied in [31] one has the ratio \( D_A/(\kappa R) \approx 2 \).

In figure 4 we plot the rescaled velocity \( V_A/(V_0 J_A) \) with \( V_A \) and \( J_A \) defined in equations (106) and (102), respectively, as a function of the catalytic coverage \( \theta_0 \). Interestingly one finds that the maximum of the absolute value of the self-propulsion velocity is attained at coverages close to \( \theta_0 = \pi/2 \) (i.e. for Janus colloids), only if the parameter \( D_A/(\kappa R) \) is sufficiently large, which corresponds to the regime of kinetic control. For small values of \( D_A/(\kappa R) \),
one finds that the maximum is shifted to values of $\theta_0$ lower than $\pi/2$, which matches with the observations we made above in section 4.2.

Further on, we focus on the special case of Janus colloids (i.e. $\theta_0 = \pi/2$ and $f^{\text{diso}}(\pi/2) \approx 0.706$) and analyze the behavior of $V_A$ in equation (106) as a function of the parameters of the triangular-well interaction potential. In figure 5 we show $V_A/V_0$ as a function of $\varepsilon_w$ for three different values of $\varepsilon_m$, and for two values of the ratio $D_A/(\kappa R)$ (i.e. two values of $R$ with $D_A$ and $\kappa$ kept at fixed values). We observe that for sufficiently small values of $\varepsilon_m$, here $\varepsilon_m = -0.1$, the contribution $V_A$ to the self-propulsion velocity $V$, generated by the interactions with the A molecules, exhibits a non-monotonic behavior. For small $\varepsilon_w$, $V_A/V_0$ is negative (hence $V$ and $F_{\text{chem}}$ have opposite signs). Upon increasing $\varepsilon_w$ it crosses 0, attains a peak value at $\varepsilon_w \approx 1.4$ (figure 5(a)) and $\varepsilon_w \approx 1.8$ (figure 5(b)), respectively, and decreases to zero for large $\varepsilon_w$. According to equation (106), this decrease is exponential in $\varepsilon_w$, which is due to the crossover to the regime of kinetic control. For larger value of $\varepsilon_m$ (e.g. $\varepsilon_m = -0.5$ in figure 5), the velocity remains negative over the whole interval $\varepsilon_w \in (0, 4)$. In principle, for such values of $\varepsilon_m$ the reduced velocity will also attain positive values and will exhibit a non-monotonic behavior, but this behavior is shifted to very large values of $\varepsilon_w$, which can be unphysical. Moreover, the peak values of $V_A$ are small. We also observe that the maximal absolute values of $V_A/V_0$ are achieved for $\varepsilon_w = 0$, which signals that the most effective self-propulsion (due to

![Figure 5](image-url)
interactions with the $A$ molecules) takes place for potentials which have a deep minimum and no repulsion at the wall, beyond the hard-wall interaction. This conclusion remains valid if the multi-species interactions are the same for all species, i.e. $J_A = J_B = J_C = J$, in which case the integral $\mathcal{J}$ will factor out (see equations (107) and (108) below). Of course, in the general case this may not hold because the contributions to $V$ stemming from different species (which appear with different signs) may compensate each other. We note, as well, that even for $J_A = J_B = J_C = J$, the sign of $V$ is not determined by the sign of $J$ but depends also on the relation between the diffusion coefficients $D_A$, $D_B$, and $D_C$.

Next we discuss the dependence of the velocity $V$ and of $F_{\text{ext}}$ (equations (72), (75) and (78)) on the size $R$ of the colloid. From our results in equations (72) and (75), we find that in leading order the self-propulsion velocity of the colloid for a reaction $A + CP \rightarrow B + CP$ is given by

$$V = -\frac{n_0 D_A}{12\beta \mu} \frac{\kappa e^{-\frac{\lambda^2}{2} R}}{\lambda^2 e^{-\frac{\lambda^2}{2} R} \sin^2(\theta_0/2) + D_A f^{(a)}_{dc}(\theta_0))}$$

$$\times \left( \frac{\lambda^2 J_A}{D_A} - \frac{\lambda^2 J_B}{D_B} \right) \sin^2(\theta_0) f^{(a)}_{dc}(\theta_0),$$

(107)

while for a dissociation reaction $A + CP \rightarrow B + C + CP$ it is given by

$$V = -\frac{n_0 D_A}{12\beta \mu} \frac{\kappa e^{-\frac{\lambda^2}{2} R}}{\lambda^2 e^{-\frac{\lambda^2}{2} R} \sin^2(\theta_0/2) + D_A f^{(a)}_{dc}(\theta_0))}$$

$$\times \left( \frac{\lambda^2 J_A}{D_A} - \frac{\lambda^2 J_B}{D_B} - \frac{\lambda^2 J_C}{D_C} \right) \sin^2(\theta_0) f^{(a)}_{dc}(\theta_0).$$

(108)

In the diffusion controlled limit (equation (97)), equations (107) and (108) reduce to

$$V = -\frac{n_0}{3\beta \mu R} \left( \frac{\lambda^2 J_A}{D_A} - \frac{\lambda^2 J_B}{D_B} \right) \cos^2(\theta_0/2) f^{(a)}_{dc}(\theta_0)$$

(109)

and

$$V = -\frac{n_0}{3\beta \mu R} \left( \frac{\lambda^2 J_A}{D_A} - \frac{\lambda^2 J_B}{D_B} - \frac{\lambda^2 J_C}{D_C} \right) \cos^2(\theta_0/2) f^{(a)}_{dc}(\theta_0),$$

(110)

respectively. In this limit one has $V \sim 1/R$. Hence, in accordance with equation (78) and in leading order, the stall force $F_{\text{ext}}$ is independent of $R$. In the kinetic control limit, equations (107) and (108) yield

$$V = -\frac{n_0}{12\beta \mu} \kappa e^{-\frac{\lambda^2}{2} R} \left( \frac{\lambda^2 J_A}{D_A} - \frac{\lambda^2 J_B}{D_B} \right) \sin^2(\theta_0)$$

(111)

and

$$V = -\frac{n_0}{12\beta \mu} \kappa e^{-\frac{\lambda^2}{2} R} \left( \frac{\lambda^2 J_A}{D_A} - \frac{\lambda^2 J_B}{D_B} - \frac{\lambda^2 J_C}{D_C} \right) \sin^2(\theta_0),$$

(112)

respectively. Therefore, in the limit of kinetic control $V$ is independent of $R$, and hence $F_{\text{ext}} \sim R$.

The dependence on $R$ predicted by our analysis is consistent with previous theoretical [97] arguments and experimental observations [31, 97] which tell that for $R$ larger than a certain threshold value the velocity $V$ decreases $\sim 1/R$ upon increasing $R$ [97], while for $R$
smaller than this threshold value the velocity saturates at a value independent of \( R \) [31]. As follows, this size dependence can be understood from the inequality in equation (97), which distinguishes between the diffusion-controlled and the kinetically-controlled regimes. For fixed physical parameters \( \kappa, \varepsilon^A, \theta_0, \) and \( D_A \), there is a threshold value of \( R \) at which equation (97) turns into an equality. For \( R \) below this threshold value, the system is in the kinetic control regime, in which \( V \) is independent of \( R \) (which is consistent with the observations in [31]). Conversely, if \( R \) exceeds the threshold value upon increasing \( R \) further, the system gradually crosses over into the diffusion control regime and, accordingly, \( V \sim 1/R \) (which agrees with the experimental results and the theoretical arguments reported in [97]).

Finally, we compare the dependences on all physical parameters of our predicted self-propulsion velocity with the results obtained in [97] for the particular case of Janus colloids, and for a diffusion-reaction model of the hydrogen peroxide dissociation in water, using the concept of the effective Derjaguin length and phoretic slip. This provides the means for a posteriori checks of the accuracy of the self-consistent approximation used for solving the diffusion equations (section 3). Before we proceed, we remark that the reaction scheme considered in [97] is slightly more complicated than the one used in our analysis: there, a two-step process has been assumed in which the hydrogen peroxide first forms a complex with the platinum (at a rate \( K_1 \)) and then, at a rate \( K_2 \), it dissociates into a water and an oxygen molecule. Our setting becomes identical to the one [97], if we consider the reaction in equation (1) (rather than the one in equation (2), because one of the reaction products is the same as the solvent) and if we set \( K_2 = \infty \) in the results of [97]. With this, our general prediction for the self-propulsion velocity is given by equation (107).

First we consider the limit \( /\theta \pi \gg R DKA_1 \). Calculating the Derjaguin length for the triangular-well potentials, we find that in the present notation the self-propulsion velocity defined by equation (8) in [97] is given by

\[
V = -0.1 \frac{n_0}{\beta \mu R} \left( \frac{\lambda^2_A J_A}{D_A} - \frac{D_A}{D_B} \frac{\lambda^2_B J_B}{D_B} \right), \tag{113}
\]

where \( J_A \) and \( J_B \) are the velocity integrals defined in equation (102) above. In view of equation (97) with \( /\theta \pi = 20 \), this limit corresponds to the regime of diffusion control, and hence, to our result in equation (109) with \( /\theta \pi = \pi/2 \). It turns out that the expression in equation (113), obtained from [97], and our prediction in equation (109) exhibit the same dependences on the diffusion coefficients of \( A \) and \( B \) molecules, the radius \( R \) of the colloid, the viscosity, and, most importantly, the same rather non-trivial dependences on the parameters of the interaction potentials. The two expressions differ only slightly with respect to the numerical prefactor: 0.1 in equation (113) and 0.117 in equation (109).

Further on, within the opposite limit \( /\theta \pi \ll R DKA_1 \), which in our analysis corresponds to the limit of reaction control, in the present notation equation (8) in [97] is given by

\[
V = -\frac{n_0}{12 \beta \mu D_A} K_1 \left( \frac{\lambda^2_A J_A}{D_A} = \frac{D_A}{D_B} \frac{\lambda^2_B J_B}{D_B} \right), \tag{114}
\]

Taking into account \( \sin^2(\pi/2) = 1 \) and identifying \( K_1 \) with \( \kappa \exp(-\varepsilon^A_\theta) \), we find perfect agreement (even concerning the numerical prefactors) between our prediction in equation (111) for \( /\theta \pi = \pi/2 \) and the prediction of [97] given by equation (114).
6. Summary and conclusions

We have studied theoretically the dynamics of a chemically active colloid, i.e. a particle which has parts of its surface decorated by a catalyst promoting a chemical reaction in the surrounding solution. We have focused on the steady state stall force needed to immobilize it or, equivalently, its self-phoretic velocity if it is free to move. As a model system we have analyzed a spherical particle with a catalytic patch (CP) forming a spherical cap with opening angle $\theta_0$. The particle is immersed in an unbounded Newtonian liquid solution, initially containing solvent ($S$) and reactant ($A$) molecules. We have considered two types of catalytically-activated reactions in which the $A$ molecules enter upon approaching the CP: either the simple conversion into product molecules $B$, i.e. $A + CP \rightarrow B + CP$, or a dissociation reaction $A + CP \rightarrow B + C + CP$. An example of the latter is the platinum catalyzed dissociation of hydrogen peroxide into oxygen and water, which is often employed in experimental studies of chemically-induced self-propulsion. All molecular species ($S$, $A$, $B$, $C$) exhibit interactions with the surface of the colloid (in addition to entering into the chemical reactions), which in general differ from species to species. Furthermore the reactant molecules and the product molecules of various species diffuse in the solution with, in general distinct, diffusion coefficients $D_A$, $D_B$, and $D_C$.

In order to derive the equations governing the steady-state dynamics, we have employed the framework of classical linear non-equilibrium thermodynamics [113]. The number densities of the reactant and product molecules are taken to be sufficiently small so that they can be considered as an ideal-gas and that the Reynolds number and the corresponding Péclet number are very small (which is valid for typical experimental setups). On this basis we have arrived (section 3) at a Smoluchowski reaction–diffusion problem with external interaction potentials (relative to the solvent one) $W_k$, $k = A, B, C$ for each species, and a Stokes flow problem with body forces determined by the distributions of molecular species and the potentials $W_k$. By generalizing a self-consistent approximation, developed originally in [102] in order to reduce the boundary conditions to the simple form of a ‘constant flux’ (section 3.3), we have solved the reaction–diffusion equations via separation of variables in spherical coordinates. The steady-state density distributions $n_k(r, \theta)$ of the various molecular species around the colloid are thus obtained in the typical form of series involving products between certain radial functions and Legendre polynomials. Interpreting the results within the chemical kinetics framework allowed us to calculate an effective reaction rate $K_{\text{eff}}$ (equation (37)) and an effective steric factor $f_{\text{dc}}(\theta_0)$ (equation (42)) for particles exhibiting non-spherical chemical reactivity. This effective reaction rate $K_{\text{eff}}$ satisfies a generalized form (equation (39)) of the well known ‘Collins and Kimball relation’.

The knowledge of the steady-state density distributions $n_k(r, \theta)$ has allowed for a straightforward calculation of the general expression for the force $\mathbf{F}_{\text{chem}}$ (equation (54)) experienced by the colloid due the interactions with the molecules in solution (i.e. species $A$, $B$, and $C$). This general expression is valid for arbitrary interaction potentials and diffusion coefficients. These density distributions correspond to an out-of-equilibrium state which is maintained by the chemical reaction. Since $\mathbf{F}_{\text{chem}}$ is only one of the contributions to the total force on the colloid (which includes also at least a hydrodynamic contribution), it is not directly measurable. But it can be accessed indirectly, e.g. by marking the molecular species and measuring their steady state distributions around the colloid with the chemical reaction switched on and off, respectively. This general expression allows one to infer various implications (section 4.2) such as the following: (i) As a function of the size $\theta_0$ of the catalyst patch, $\mathbf{F}_{\text{chem}}$ is non-monotonic and exhibits a maximum magnitude for an angle $\theta_0$ which in general differs from $\pi/2$. (ii) The direction of $\mathbf{F}_{\text{chem}}$ depends on the relative magnitude of the various diffusion coefficients.
The use of the reciprocal theorem [108, 109] facilitates to express the main quantities of interest, i.e. the stall force $F_{\text{ext}}$ and the self-propulsion velocity $V$ (which are both directly measurable), solely in terms of the contribution $n = 1$ of the series representations of the densities $\theta_n(r, \theta)$ (equations (78) and (72)). The direct calculations of the hydrodynamic force exerted on the colloid (via determining the flow of the solution) turned out to be a rather challenging problem. Since this is not playing a crucial role in the present study, we leave this issue to future studies.

The general theoretical framework established here is illustrated by choosing so-called triangular-well potentials as examples of the basic underlying interaction potentials $W_j(r)$. These potentials are characterized for each of the species by a fixed value $W_j(R)$ of the potential at the wall (i.e. the colloid surface), by the well depth $W_j(R + \lambda_j)$ at $r = R + \lambda_j$, and by being truncated at $r = R + \Lambda_j$, $j = A, B, C$. In the physically relevant limit $\lambda_j/R \ll 1$, with $\lambda_j/\Lambda_j$ kept fixed, this choice of the interaction potentials allows one to obtain analytic expressions for $F_{\text{chem}}$, $F_{\text{ext}}$, and $V$ in leading order in $\lambda_j/R$.

This analysis reveals that the behavior of $F_{\text{chem}}$ is dominated by the values $W_j(R)$ of the potentials at the wall, while the behavior of the self-propulsion velocity $V$ and of the stall force $F_{\text{ext}}$ depends primarily on the depths $W_j(R + \lambda_j)$ of the potential wells. These expressions predict that within certain parameter ranges $F_{\text{chem}}$ and $V$ may have opposite signs; the same sign occurs for sufficiently strong repulsive interactions with the wall. In general, it appears that not only the calculation of the values of $F_{\text{chem}}$ and $V$, but even determining their signs, is a rather complicated problem which involves all interaction parameters and all diffusion coefficients. Our analysis shows that, similarly to $F_{\text{chem}}$, $F_{\text{ext}}$ and hence $V$ attain, in general, as functions of $\theta_0$ their maximal values for $\theta_0$ close to but not exactly at $\pi/2$ (Janus particles); only in the limit of kinetic control the maximum of these properties is attained exactly at $\theta_0 = \pi/2$. Finally, we have found that for sufficiently small colloids the propulsion velocity is independent of their size. For large colloids, $V$ decreases with their size as $1/R$. Our conclusions concerning the dependence of $V$ on $R$ are consistent with previous theoretical arguments and experimental observations [31, 97]. Lastly, we have shown that, for short-ranged triangular-well potentials, in two limiting situations (the reaction control and the diffusion control regimes) our general results reproduce the results obtained in [97] by using the concepts of the effective Derjaguin length and phoretic slip.

There are several directions along which generalizations of the approach developed here are feasible and could provide significant physical insight. First, one can invoke more involved contributions of the catalyst to the reaction scheme, for example the formation of catalyst-bound activated complexes with finite lifetimes, as considered in [97]. Second, it is plausible that the dissociation reaction at the catalyst is accompanied by recombination or annihilation of some (or all) of the products in the bulk solution or in a different region on the surface of the particles; such systems can be expected to exhibit a significantly richer behavior resulting from the interplay between the different time- and length-scales of the various reactions. Third, since most of the experimental studies of chemically active colloids involve particles suspended in (weak) electrolytes and reactions which are expected to produce ionic radicals, it is natural to consider extending the approach developed here by adding to the present description the corresponding equations which account for charge conservation. Last but not least, the influence of rotational diffusion of an active particle on the stall force or on the self-propulsion velocity can be straightforwardly included into the framework presented here.

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Appendix A. Spatial distribution of the molecular components of the mixture

We aim at describing the distribution of the molecular components in the mixture within the standard theory of linear non-equilibrium thermodynamics [93, 101, 113, 114]. The solution as a whole is assumed to behave as an incompressible Newtonian fluid. The reaction will be accounted for via boundary conditions on the surface of the colloid. Therefore, the description of the dynamics of the mixture will involve (i) continuity equations (conservation of mass) for the mixture and for the A and B species; (ii) linear relations between the conjugate thermodynamic fluxes and forces determining the entropy production rate; (iii) the Navier–Stokes equations obeyed by the barycentric velocity $\mathbf{u}(\mathbf{r})$ of the mixture (i.e. conservation of momentum).

The liquids involved in typical experimental studies have a very low compressibility; therefore they can be assumed to have a constant mass density $\rho = \text{const}$. (For a discussion of the more general case in which this assumption is softened one can consult, e.g. [92].)

In terms of the number densities $n_A$, $n_B$, and $n_S$ and the molecular masses, and accounting for the fixed number densities of $A$ and $S$ molecules far from the colloid, this can be expressed as

$$\rho(\mathbf{r}, t) = \rho = n_A(\mathbf{r}, t) m_A + n_B(\mathbf{r}, t) m_B + n_S(\mathbf{r}, t) m_S$$

where the rhs corresponds to $\rho(\mathbf{r}, t = 0)$. The local number density of the solvent can be determined once $\rho$ and the number densities of the A and B species are known.

Considering total mass conservation in a small volume element $\delta V$ located at $\mathbf{r}$ (which, however, is sufficiently large to contain a large number of $A$, $B$, and $S$ molecules such that their number densities in $\delta V$ are well defined) leads to the continuity equation for the mixture:

$$\frac{\partial \rho}{\partial t} + \nabla (\rho \mathbf{u}) = 0 \quad \Rightarrow \quad \nabla \mathbf{u} = 0,$$

(A.2)

where $\rho \mathbf{u}$ is the mass current density or the momentum density; $\mathbf{u}$ is the barycentric velocity, i.e. the momentum density divided by the mass density.

Assuming local equilibrium, the free energy $F(T, V, N_A, N_B, N_S)$ of the isothermal fluid mixture in contact with the colloidal particle can be written in terms of a local free energy density (per volume) $f(T, n_A := \delta N_A/\delta V, n_B := \delta N_B/\delta V, n_S := \delta N_S/\delta V)$ as $F = \int_V f dV$, where

$$df = -s dT + \tilde{\mu}_A dN_A + \tilde{\mu}_B dN_B + \tilde{\mu}_S dN_S.$$

(A.3)

In the expression above $s := \delta S/\delta V$ is the local entropy density, $\delta N_A(B,S)$ is the number of $A (B, S)$ molecules, respectively, in the volume $\delta V$ and the interactions with the colloid have been accounted for by the modified chemical potentials [113]

$$\tilde{\mu}_j := \mu_j + \Phi_j, \quad j = A, B, S.$$

Note that while the modified chemical potentials $\tilde{\mu}_j$ are taken to be constant over the small volume element $\delta V$, they vary spatially. This is the case because the interaction potentials $\Phi_j$ vary spatially and the chemical potentials $\mu_j$ (in the absence of interactions) vary with position due to the fluid mixture being in contact with the source (sink) for the $B$ ($A$) species at the colloid surface and with the sink (source) for the $B$ ($A$) species far away from the colloid surface so that the system is out of thermodynamic equilibrium.

The incompressibility condition in equation (A.1) implies that only two of the densities $n_A$, $n_B$, and $n_S$ are independent. In order to connect straightforwardly to the continuity equations (i.e. mass conservation) in $\delta V$ for each of the molecular species (see the next paragraphs), it is advantageous to change the variables from number densities to concentrations, i.e. mass fractions, which are defined as
\[ c_j(\mathbf{r}, t) := \frac{\rho_j(\mathbf{r}, t)}{\rho} = \frac{m_j n_j(\mathbf{r}, t)}{m_A n_A(\mathbf{r}, t) + m_B n_B(\mathbf{r}, t) + m_S n_S(\mathbf{r}, t)}, \quad j = A, B, S. \tag{A.5} \]

Here \( \rho(\mathbf{r}, t) = m_j \rho_j(\mathbf{r}, t) \) denotes the mass density of species \( j = A, B, S \). The concentrations obey the relation \( c_A + c_B + c_S = 1 \). With \( d n_j = (\rho m_j) \, d c_j \) and \( d c_S = -(d c_A + d c_B) \), equation (A.3) takes the form

\[ df = -sdT + \tilde{\mu}_A d c_A + \tilde{\mu}_B d c_B. \tag{A.6} \]

The chemical potentials \( \tilde{\mu}_j \) conjugated to the concentration variables are given by

\[ \tilde{\mu}_j := \left( \frac{\tilde{\rho}_j}{m_j} - \frac{\tilde{\rho}_S}{m_S} \right) \rho = \left( \frac{\tilde{\rho}_j}{m_j} - \frac{\tilde{\rho}_S}{m_S} \right) \rho + \frac{W_j}{m_j} \rho, \quad j = A, B. \tag{A.7} \]

Therefore the mixture is described completely by \( c_A(\mathbf{r}) \) and \( c_B(\mathbf{r}) \); \( c_S(\mathbf{r}) \) follows from the incompressibility condition in equation (A.1).

The local mass conservation for the species \( A \) and \( B \) in the region outside the impermeable sphere \( (r > R) \) implies that the concentrations \( c_{A,B}(\mathbf{r}, t) \) obey the continuity equations \[113\] (see equation (A.5))

\[ \frac{\partial (\rho c_j)}{\partial t} + \nabla \cdot \mathbf{J}_j = 0, \quad j = A, B, \tag{A.8} \]

where, in line with the usual non-equilibrium thermodynamics framework \[38, 113\], the currents \( \mathbf{J}_{A,B} \) are split into a convective part due to the barycentric motion and a ‘diffusion’ part \( \mathbf{j}_{A,B} \) due to the motion relative to that of the local center of mass:

\[ \mathbf{J}_j := \rho \mathbf{c}_j \mathbf{u} + \mathbf{j}_j, \quad j = A, B, \tag{A.9} \]

where \( \mathbf{u} \) is the center of mass (barycentric) velocity of the mixture in the volume element \( \delta V \).

The advantage of the decomposition in equation (A.9) is that within the framework of linear non-equilibrium thermodynamics the currents \( \mathbf{j}_j \) are the ‘fluxes’ coupled to the thermodynamic forces which, in accordance with the expression for the entropy production (see \[113\]), are given by the spatial gradients of the chemical potentials \( \tilde{\mu}_j \) introduced in equation (A.7).

Therefore, each of the \( \mathbf{j}_j \) can be written as a linear combination of these gradients \[113\]:

\[ \mathbf{J}_A = -\frac{L_{AA}}{T} \nabla \tilde{\mu}_A - \frac{L_{AB}}{T} \nabla \tilde{\mu}_B, \]
\[ \mathbf{J}_B = -\frac{L_{BB}}{T} \nabla \tilde{\mu}_B - \frac{L_{BA}}{T} \nabla \tilde{\mu}_A, \tag{A.10} \]

where \( T \) is the temperature (assumed to be spatially constant) and the couplings \( L_{AA} > 0, L_{BB} > 0, \) and \( L_{AB} = L_{BA} \) are the so-called Onsager coefficients.

Furthermore, since we consider low concentrations, so that there are effectively no interactions between the \( A \) and \( B \) species, we shall disregard the possibility of a direct influence of the dynamics of \( B \) on that of \( A \). Therefore we disregard the possibility that currents of \( A \) are directly driven by gradients of the concentration and thus of the chemical potential \( \tilde{\mu}_B \) of the \( B \) molecules. Thus we set \( L_{AB} = 0 \). (In the context of active colloids, the conditions under which this assumption is expected to hold are discussed in more detail in \[92\].) Although these cross-terms are sometimes important even for dilute solutions \[113\], our use of this approximation is...
motivated by previous reports showing that in many cases the diffusion coefficients (accounting for currents driven by concentration gradients, which are the most relevant terms in our system) in ternary mixtures are such that the cross-terms induced contributions are much smaller than the ones due to self-diffusion [115–120]. (But we note that recently for a ternary mixture cross-term diffusion coefficients have been reported which are of the same order of magnitude as the self-diffusion ones [121]; however, this was found for comparable concentrations and thus far from the dilute solution limit we are considering here.)

Within this approximation one has

\[ \mathbf{j}_A = -\frac{\rho L \Delta A}{T} \nabla \left( \frac{\mu_A}{m_A} - \frac{\mu_S}{m_S} \right) - \frac{\rho L \Delta A}{T} \nabla \left( \frac{W_A}{m_A} \right) \]  

(A.11)

and the analogous expression for \( \mathbf{j}_B \) in which \( A \) is replaced by \( B \). This expression shows that the influence of the external interaction potentials has been isolated into a single contribution (the last term on the right hand side of equation (A.11)). The mass current is now decomposed into a contribution solely due to the composition of the mixture (i.e. the first term on the right hand side of equation (A.11)) and a convective part solely due to the difference \( W_A \) (\( W_B \)) between the interaction of the \( A(B) \) molecules with the colloid and the interaction, weighted by the corresponding mass ratio \( m_{A,B}/m_S \), of the \( S \) molecules with the colloid.

Under the above assumption, the chemical potentials \( \hat{\mu}_A \) and \( \hat{\mu}_B \) with

\[ \hat{\mu}_{A,B} := \frac{\mu_{A,B}}{m_{A,B}} - \frac{\mu_S}{m_S} \]  

(A.12)

are functions (see equation (A.6)) of the temperature \( T \) (assumed to be spatially constant for our system) and of the local concentration \( c_A \) of the \( A \) molecules (\( \hat{\mu}_A \)) or of the concentration \( c_B \) of the \( B \) molecules (\( \hat{\mu}_B \)), respectively. Explicit expressions for these dependences would require knowledge of the free energy density, i.e. a specific model of the mixture. However, further progress can be made by arguing that, because the concentrations of \( A \) and \( B \) molecules are assumed to remain very small at all times and the mixture is incompressible, the spatial variations of the chemical potential of the solvent \( \mu_S \) can be neglected relative to those of the chemical potentials of the solutes. This is so because for an ideal dilute solution the chemical potential of the solute is proportional to the logarithm of the solute concentration, while that of the solvent is proportional to the solute concentration (see chapter IX in [114]).

This implies that \( \nabla (\hat{\mu}_A) \gamma \sim \frac{\nabla c_A}{c_A} \) while \( \nabla (\hat{\mu}_B) \gamma \sim \nabla (c_A + c_B) \), and thus the magnitude of the former is greater than that of the latter by a factor \( 1/c_{A,B} \), which is very large. Therefore, for a dilute solution one can approximate \( \nabla (\hat{\mu}_{A,B}) \gamma \sim \frac{\nabla c_{A,B}}{m_{A,B}} \) [114], where \( k_B \) is the Boltzmann constant. Accordingly the decomposition in equation (A.11) implies that the diffusion (relative motion) part of the particle current can be written as the superposition of concentration gradients and convective terms (which are due to the external fields), for which one can directly formulate the usual expression [113]

\[ \mathbf{j}_{A,B} = -D_{A,B} \left[ \nabla (\rho c_{A,B}) + \beta \rho c_{A,B} \nabla W_{A,B} \right]. \]  

(A.13)

Here \( \rho \) is constant, \( \beta = 1/(k_B T) \), and \( D_{A,B} = (k_B L_{AA,BB})/(m_{A,B} c_{A,B}) \) are the heuristically defined diffusion coefficients of the \( A \) and \( B \) species, respectively. They are expressed in terms of the unknown Onsager coefficients \( L_{AA} \) and \( L_{BB} \) and, in general, the partial derivatives of the chemical potentials \( \hat{\mu}_{A,B} \) with respect to the corresponding concentrations at constant temperature. We note that the diffusion coefficients \( D_{A,B} \) defined above and entering in equation (A.13) are the so-called ‘collective diffusion’ coefficients, which, in general,
are different from the single particle ones, introduced in section 2, which are describing the mean-square displacement of the Brownian motion of $A$ ($B$) molecules. However, in the dilute limit, which is the case considered in this study, the two quantities coincide, thus the use of the same notation.

Using the expression in equation (A.13), the total particle current in equation (A.9) has the form ($\rho_j = \rho_c n_j$, equation (A.5))

$$
\mathbf{J}_J = \rho_j \mathbf{u} - D_j (\nabla \rho_j + \rho_j \nabla (\beta W_j)) = \frac{D_j \rho_j}{R} \left( \frac{U_j R}{D_j} c_j U - \nabla c_j - c_j \nabla (\beta W_j) \right), \quad j = A, B, 
$$

(A.14)

where $U_0$ denotes a typical velocity scale for the flow of the mixture, $\xi = r/R$, and $\mathbf{U} = \mathbf{u}/U_0$.

In the following we make the additional assumption that for the systems of interest the Péclet number $\text{Pe} = UrD/D_0$ is much smaller than 1 and thus the effects of the barycentric convection are negligible. As previously reported, this is indeed the case for catalytically active colloids, for which typical Pe numbers are $\text{Pe} \lesssim 10^{-2}$ [9, 43, 93]. With this final approximation, after inserting equation (A.14) into the equation (A.8), one obtains that the concentrations ($\rho_c n_j$, equation (A.15)) obey the following diffusion equations:

$$
\frac{\partial c_j}{\partial t} = D_j \nabla \cdot \left( \nabla c_j + \beta c_j \nabla W_j(r) \right) + D_j \nabla \cdot \left[ e^{-\beta W_j(r)} \nabla (e^{\beta W_j(r)} c_j) \right], \quad j = A, B.
$$

(A.15)

Due to $c_j = (m_j/\rho)n_j$ and owing to the assumption of negligible cross-term diffusion (see equations (A.10) and (A.11)), the dynamics of the concentrations of the different species are effectively decoupled. Accordingly, with $c_j = (m_j/\rho)n_j$, equation (A.15) can be transcribed in terms of the number density fields, which is a more convenient representation for the system under study (see section 4), and yields equation (4).

**Appendix B. Catalytically induced dissociation**

Here we present, using our results in section 3.3, the derivation of the spatially inhomogeneous, steady state distribution of the product molecules $C$, which emerge in the catalytically induced dissociation reaction described in equation (2).

As in section 3.3, we suppose that the product molecules $C$ of mass $m_C$ diffuse with the diffusion coefficient $D_C$ and interact with the colloid via a radially symmetric potential $W_C(r)$ (relative to that of the solvent molecules, similar to the definition in equation (3) for the $A$ and $B$ molecules). Accordingly, the time evolution of the local density of the reaction product $C$ obeys the differential equation

$$
0 = \frac{D_C}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial n_C}{\partial r} \right) + \frac{\beta D_C}{r^2} \frac{\partial}{\partial r} \left( r^2 n_C \frac{dW_C}{dr} \right) + \frac{D_C}{r^2 (\sin \theta)} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial n_C}{\partial \theta} \right), \quad 0 < \theta < \pi.
$$

(B.1)

which has the same form as equations (5) and (40). Similarly to equation (40), which describes the time evolution of the reaction product $B$, equation (B.1) is to be solved subject to a sink boundary condition at macroscopic distances from the colloid (as in equation (41)) and subject to the mixed boundary conditions imposed at the surface of the colloid: the zero current
condition at the inert part of the surface and the reactive boundary condition at the catalytically active patch (as in equation (42) with $B$ replaced by $C$).

According to the assumptions of the present model the dynamics of $C$ is decoupled from that of $B$. (Interactions between $B$ and $C$ and between $A$ and $B$ as well as $A$ and $C$ would change this.) Therefore all results for the $B$ species obtained in the previous section can be simply transcribed to the present case with the replacements $B \rightarrow C$ and $j_n \rightarrow h_n$ (see below).

In line with equation (43), the steady state distribution of the product $C$ has the form

$$n_C(r, \theta) = n_0 e^{-\beta W(r)} \sum_{n=0}^{\infty} \gamma_n h_n(r) P_n(\cos \theta),$$

where the functions $h_n(r)$ are those solutions of (compare equation (44))

$$h_n''(r) + \left( \frac{2}{r} - \beta W(r) \right) h_n'(r) - \frac{n(n+1)}{r^2} h_n(r) = 0,$$

which vanish for $r \rightarrow \infty$ and are normalized such that $h_n(r = R) = 1$. The dimensionless coefficients $\gamma_n$ are given by (see equation (45))

$$\gamma_n = -\frac{Q}{2 D_c n_0} \frac{e^{\beta W(R)}}{h_n'(R)} \phi_n(\theta_0)$$

$$= -\frac{K_{\text{eff}}}{4 \pi D_c R} \frac{e^{\beta W(R)}}{h_n'(R)} \phi_n(\theta_0), \quad n \geq 0.$$

As in equation (46), in the diffusion-controlled limit one has

$$\gamma_n(K^* \rightarrow \infty) = -\frac{D_A}{D_c} \frac{R D}{R} \frac{e^{\beta W(R)}}{h_n'(R)} \phi_n(\theta_0) f_k(\theta_0), \quad n \geq 0,$$

while in the limit of kinetic control the coefficients $\gamma_n$ are given by (equation (47))

$$\gamma_n(D_\Lambda \rightarrow \infty) = -\frac{K^*}{4 \pi D_c R} \frac{e^{\beta W(R)}}{h_n'(R)} \phi_n(\theta_0), \quad n \geq 0,$$

and, in this limit, are independent of $D_\Lambda$.

**Appendix C. The generalized reciprocal theorem of Teubner**

For an easier understanding, here we include a brief derivation of the generalized reciprocal theorem due to Teubner [109], which we use in order to determine the velocity of the self-propelled colloid (equation (71)). For a detailed discussion, as well as various applications of this result, the interested reader is referred to the original paper [109] or the textbook by Kim and Karrila [108].

By applying the equivalent of Gauss’ theorem for tensor fields [138] and selecting the orientation of the surface elements entering into the surface integral to be the one given by the inner normals, for arbitrary tensor fields $\mathbf{\hat{I}}$ and arbitrary vector fields $\mathbf{u}'$ one obtains

$$\int_D \nabla \cdot (\mathbf{u}' \cdot \mathbf{\hat{I}}) \, d\mathbf{r} = -\int_{\partial D} \mathbf{u}' \cdot \mathbf{\hat{I}} \cdot ds - \int_{S_{\infty}} \mathbf{u}' \cdot \mathbf{\hat{I}} \cdot ds_{\infty} = -\int_{\partial D} \mathbf{u}' \cdot \mathbf{\hat{I}} \cdot ds.$$
\( \mathcal{D} \) is that domain in \( \mathbb{R}^3 \) which on the inner side is bounded by a closed surface \( \partial \mathcal{D} \) (such that \( \mathcal{D} \) is the exterior of \( \partial \mathcal{D} \)) and on the outer side by the surface \( S_\infty \) of an enclosing large sphere with radius \( R_\infty \), which extends to infinity. The integral over \( S_\infty \) vanishes for \( R_\infty \to \infty \) if \( \mathbf{u}' \) and \( \hat{\mathbf{t}} \) decay sufficiently rapidly upon increasing the distance from \( \mathcal{D} \); this is the case for the hydrodynamic flows we are interested in, for which \( |\mathbf{u}'(r \gg 1)| \sim 1/r \) or faster. A similar relation follows from swapping the primed and unprimed fields. In the following, \( \mathbf{u} \) and \( \hat{\mathbf{t}} \), as well as the corresponding primed quantities, are taken to be the velocity and pressure fields, respectively, entering into the Stokes equations (equations (48) and (49)).

In order to prove the proposition in equation (65) we first consider its left hand side which can then be transformed as follows (note that here Einstein’s convention of summation over repeated indices is used):

\[
\begin{align*}
\mathcal{A} := \mu' \int_D \mathbf{u}' \cdot \hat{\mathbf{t}} \cdot ds &= \int_D \mathbf{u}' \cdot \mathbf{f} \, d^3r \\
&= \mu' \int_D \left[ -\nabla \cdot (\mathbf{u}' \cdot \hat{\mathbf{t}}) - \mathbf{u}' \cdot \mathbf{f} \right] \, d^3r \\
&= \mu' \int_D \left[ -\nabla \cdot \left( \partial \mathbf{u} \hat{\mathbf{t}} \right) - \mathbf{u}' \cdot \mathbf{f} \right] \, d^3r \\
&= \mu' \int_D \left[ \nabla \cdot \left( \partial \mathbf{u} \hat{\mathbf{t}} \right) + \mathbf{u}' \cdot \mathbf{f} \right] \, d^3r \\
&= \mu' \int_D \left[ \nabla \cdot \left( \partial \mathbf{u} \hat{\mathbf{t}} \right) + \mathbf{u}' \cdot \mathbf{f} \right] \, d^3r \quad \text{(equation (48))}
\end{align*}
\]

As stated above, equation (C.1) also holds after swapping the primed and unprimed fields (because they are defined in the same domain and are assumed to decay sufficiently rapidly at infinity). Therefore a similar sequence of transformations as in equation (C.2) can be applied to the rhs of equation (65). Since the last line in equation (C.2) is invariant with respect to interchanging the primed and unprimed quantities, one concludes that the lhs and the rhs are equal, so that equation (65) holds.

**Appendix D. Triangular-well interaction potentials**

In this appendix we summarize the derivations of the results presented in section 5 for the particular choice of triangular-well interaction potentials, which are defined by equations (81) and (84) and depicted in figure 2. By focusing on the interaction between the colloid and the molecules of species \( A \) we determine the corresponding Debye radius \( R_D \) (equation (17)), the radial functions \( g_0(r) \) and \( g_1(r) \) (equation (15)), as well as their derivatives at the wall (i.e. at the colloid surface \( r = R \)). From these quantities we obtain the force integral \( I_A \) (equation (55)) and the velocity integral \( J_A \) (equation (73)). The corresponding quantities associated with the interactions between the colloid and the species \( B \) and \( C \) are obtained by simply replacing the labels: \( A \to B \) or \( A \to C \). Finally, in the leading order in \( \lambda_n/R \ll 1 \), we determine the expression for the first derivative at the wall of the radial functions \( g_n(r) \) for arbitrary \( n > 1 \). This allows us to infer the asymptotic behavior of the steric factor \( f_{L}(\theta_0) \) (equation (31)) for \( \lambda_n/R \ll 1 \).
D.1. Debye radius

For triangular-well interaction potentials equation (17) yields

\[
R_D^{-1} = \exp\left(\varepsilon_m^A + \Delta \varepsilon_A \frac{R}{\lambda_A}\right) \int_R^{R+\lambda_A} \frac{dr}{r^2} \exp\left(-\Delta \varepsilon_A \frac{r}{\lambda_A}\right) \\
+ \exp\left(\frac{(R + \Lambda_A)}{(\Lambda_A - \lambda_A)} \varepsilon_m^A\right) \int_{R+\lambda_A}^{R+\Lambda_A} \frac{dr}{r^2} \exp\left(-\frac{\varepsilon_m^A}{(\Lambda_A - \lambda_A)} r\right) + \int_{R+\Lambda_A}^{\infty} \frac{dr}{r^2}.
\] (D.1)

The integrals in equation (D.1) can be calculated analytically and lead to a rather cumbersome combination of exponential integrals. Focusing on the physically relevant limit \(\lambda_A \ll R\) (i.e. \(q_A = \lambda_A/R \ll 1\)) and \(\Lambda_A \ll R\) (i.e. \(Q_A = \Lambda_A/R \ll 1\)) while the ratio \(z_A = \Lambda_A/\lambda_A > 1\) is fixed (see figure 2), from equation (D.1) one finds that in leading and first sub-leading order in \(q_A\) the Debye radius is given by

\[
\frac{R_D}{R} = 1 - \frac{[\Delta \varepsilon_A - \varepsilon_m^A e^{\varepsilon_m^A} + \varepsilon_m^A e^{\varepsilon_m^A} - \Delta \varepsilon_A z_A (1 + \varepsilon_m^A - e^{\varepsilon_m^A})]}{\varepsilon_m^A \Delta \varepsilon_A} q_A.
\] (D.2)

In equation (D.2) the first sub-leading term can be positive or negative, depending on whether the attractive or the repulsive part of the interaction potential dominates. In particular, for small values of \(\varepsilon_m^A\) and \(\varepsilon_m^A\) the expansion of the exponentials in equation (D.2) in terms of power series up to second order in these parameters renders

\[
\frac{R_D}{R} = 1 - \frac{\varepsilon_m^A + z_A \varepsilon_m^A}{2} q_A.
\] (D.3)

This implies that, for small values of \(\varepsilon_m^A\) and \(\varepsilon_m^A\) one has \(R_D < R\) if \(\varepsilon_m^A > z_A |\varepsilon_m^A|\), i.e. the repulsive part of the interaction potential dominates, while one has \(R_D > R\) for \(\varepsilon_m^A < z_A |\varepsilon_m^A|\), i.e. if the attractive part of the interaction potential prevails.

D.2. The solution of equation (15) for \(n = 0\) and its derivative at the surface

Since the potential \(W_A(r)\) is a piece-wise continuous function of \(r\), which has different functional forms in the inner \((r \in (R, R + \lambda_A))\), intermediate \((r \in (R + \lambda_A, R + \Lambda_A))\), and outer \((r \in (R + \Lambda_A, \infty))\) regions, respectively, we solve equation (15) for each region and connect the pieces by requiring the continuity of the solution and of its first derivative at the two connecting points between the three intervals. In the following we denote the solutions of equation (15) (for general \(n\)) in the corresponding intervals as \(g_n^i(r), g_n^i(r)\), and \(g_n^o(r)\) for the inner, intermediate, and outer interval, respectively.

For \(n = 0\) and with \(W_A(r)\) given by equations (81), (84) and (86) equation (15) leads to

\[
g_0^{<}(r) = C_0^{(1)} f_{1,0}(r) + C_0^{(2)} f_{0,0}(r), \quad g_0^{>}(r) = C_0^{(3)} f_{1,0}(r) + C_0^{(4)} f_{0,0}(r), \quad g_0^{>}(r) = C_0^{(5)} \frac{R}{r}
\] (D.4)

where we have introduced
with \( \text{Ei}(\cdot) \) denoting the exponential integral [141].

The constants \( C_k^0, k = 1, 2, \ldots, 5 \), are determined from the boundary and the continuity conditions: \( g_0(R) = 1 \) with \( g_0(r) \) and \( g_0'(r) \) continuous at \( r = R + \lambda_A \) and \( r = R + \Lambda_A \). These conditions lead to

\[
f_1,0(r) = -\frac{\epsilon_m^A}{(\lambda_A - \lambda_A)} \text{Ei}\left(-\frac{\epsilon_m^A}{(\lambda_A - \lambda_A)} r\right) - \frac{1}{r} \exp\left(-\frac{\epsilon_m^A}{(\lambda_A - \lambda_A)} r\right),
\]

\[
F_{1,0}(r) = \frac{\Delta \epsilon_A}{\lambda_A} \text{Ei}\left(-\frac{\Delta \epsilon_A}{\lambda_A} r\right) + \frac{1}{r} \exp\left(-\frac{\Delta \epsilon_A}{\lambda_A} r\right),
\]

(D.5)

where \( \text{Ei}(\cdot) \) and \( \lambda_A = q_A/R \) and

\[
C_0^{(1)} = \frac{f_1,0'(r)|_{r=R+\lambda_A}}{L_0(\lambda_A, \Lambda_A)}, \quad C_0^{(2)} = 1 - \frac{F_{1,0}(r)|_{r=R+\lambda_A}}{L_0(\lambda_A, \Lambda_A)}, \quad C_0^{(3)} = \frac{f_1,0'(r)|_{r=R+\lambda_A}}{L_0(\lambda_A, \Lambda_A)},
\]

\[
C_0^{(4)} = -\frac{f_1,0'(r)|_{r=R+\lambda_A} F_{1,0}(r)|_{r=R+\lambda_A}}{L_0(\lambda_A, \Lambda_A)}, \quad C_0^{(5)} = -\frac{R(1 + Q_A) f_1,0'(r)|_{r=R+\lambda_A}}{L_0(\lambda_A, \Lambda_A)},
\]

(D.6)

where \( Q_A = \Lambda_A/R \) and

\[
L_0(\lambda_A, \Lambda_A) = (F_1,0(R) - F_1,0(R + \lambda_A)) f_1,0'(r)|_{r=R+\lambda_A}
\]

\[
+ \left( f_1,0(R + \lambda_A) - f_1,0(R + \Lambda_A) - R(1 + Q_A) f_1,0'(r)|_{r=R+\lambda_A} \right) F_{1,0}(r)|_{r=R+\lambda_A}.
\]

(D.7)

The derivative of \( g_0(r) \) at the wall (i.e. \( r = R \)) is thus given by

\[
g_0'(R) = \left( \frac{d}{dr} g_0(r) \right)|_{r=R} = \frac{f_1,0'(r)|_{r=R+\lambda_A}}{L_0(\lambda_A, \Lambda_A)} = -\frac{\Delta \epsilon_A}{\lambda_A} \frac{\epsilon_m^A e^{\Delta \epsilon_A}}{R L_0(\lambda_A, \Lambda_A)}
\]

(D.8)

where \( q_A = \lambda_A/R, z_A = Q_A, Q_A = \Lambda_A/R, \) and

\[
L_0 = \frac{(e^{\Delta \epsilon_A}(1 + q_A)^2 - 1) \epsilon_m^A + (z_A - 1) \Delta \epsilon_A q_A}{(1 + q_A)^2} + e^{-\epsilon_m^A q_A + \epsilon_m^A} + (\epsilon_m^A - 1) z_A q_A \Delta \epsilon_A
\]

\[
+ \frac{1}{(1 + z_A q_A)^2}.
\]

(D.9)

For \( q_A \ll 1 \), in leading and first sub-leading order equation (D.8) renders

\[
g_0'(R) = -\frac{\epsilon_m^A}{R} + \frac{1}{\epsilon_m^A} \epsilon_m^A (e^{\Delta \epsilon_A} - 1) + \Delta \epsilon_A (1 - e^{\epsilon_m^A})
\]

\[
+ z_A \Delta \epsilon_A (1 - e^{\epsilon_m^A}) \frac{e^{\epsilon_m^A} \Delta \epsilon_A}{\epsilon_m^A q_A}.
\]

(D.10)

The second term in equation (D.10) vanishes for \( \Delta \epsilon_A = 0 \) as well as for \( \epsilon_m^A = 0 \).
D.3. The solution of equation (15) for \( n \geq 1 \)

For \( n \geq 1 \), the solutions \( g_n^\infty(r), g_n^I(r), \) and \( g_n^\Omega(r) \) of equation (15) corresponding to the inner, intermediate, and outer region, respectively, are given by

\[
g_n^\infty(r) = C_n^{(1)} F_{1,n}(r) + C_n^{(2)} F_{2,n}(r), \quad g_n^I(r) = C_n^{(3)} f_{1,n}(r) + C_n^{(4)} f_{2,n}(r),
\]

\[
g_n^\Omega(r) = C_n^{(5)} \left( \frac{R}{r} \right)^{n+1}, \tag{D.11}
\]

where

\[
F_{1,n}(r) = r^n \exp \left( - \frac{\varepsilon_A}{\lambda_A} r \right) U \left( n + 2, 2n + 2; \frac{\varepsilon_A}{\lambda_A} r \right),
\]

\[
F_{2,n}(r) = r^n \exp \left( - \frac{\varepsilon_A}{\lambda_A} r \right) M \left( n + 2, 2n + 2; \frac{\varepsilon_A}{\lambda_A} r \right),
\]

\[
f_{1,n}(r) = r^n U \left( n, 2n + 2; -\frac{\varepsilon_A}{\lambda_A - \lambda_A} r \right),
\]

\[
f_{2,n}(r) = r^n M \left( n, 2n + 2; -\frac{\varepsilon_A}{\lambda_A - \lambda_A} r \right), \tag{D.12}
\]

with \( M(\cdot) \) and \( U(\cdot) \) as Kummer’s and Tricomi’s hypergeometric function, respectively [141].

The coefficients \( C_n^{(k)} \) are spatially constant and determined by the boundary and the continuity conditions (similar to the case \( n = 0 \)). We find that the constants \( C_n^{(k)}(n \geq 1) \) are given by the following explicit (albeit rather lengthy) expressions:

\[
C_n^{(1)} = \frac{f_{1,n}(R + \lambda_A) f_{2,n}^{(2)}(L_\lambda^{(2)} - L_\Lambda^{(2)}) - f_{2,n}(R + \lambda_A) f_{1,n}^{(1)}(L_\lambda^{(2)} - L_\Lambda^{(2)})}{f_{1,n}(R + \lambda_A) f_{2,n}(R + \lambda_A) L_n(\lambda_A, \lambda_A) - f_{2,n}(R + \lambda_A) f_{1,n}(R + \lambda_A) L_n(\lambda_A, \lambda_A)},
\]

\[
C_n^{(2)} = \frac{f_{2,n}(R + \lambda_A) f_{2,n}^{(1)}(L_\lambda^{(1)} - L_\Lambda^{(1)}) - f_{2,n}(R + \lambda_A) f_{1,n}^{(1)}(L_\lambda^{(2)} - L_\Lambda^{(1)})}{f_{2,n}(R + \lambda_A) f_{2,n}(R + \lambda_A) L_n(\lambda_A, \lambda_A) - f_{2,n}(R + \lambda_A) f_{1,n}(R + \lambda_A) L_n(\lambda_A, \lambda_A)},
\]

\[
C_n^{(3)} = \frac{f_{1,n}(R + \lambda_A) f_{2,n}^{(2)}(L_\lambda^{(2)} - L_\Lambda^{(1)})}{f_{1,n}(R + \lambda_A) L_n(\lambda_A, \lambda_A)}, \quad C_n^{(4)} = -\frac{f_{1,n}(R + \lambda_A) f_{2,n}(R + \lambda_A) L_n(\lambda_A, \lambda_A)}{f_{2,n}(R + \lambda_A) L_n(\lambda_A, \lambda_A)}, \quad C_n^{(5)} = \frac{(1 + Q_A) n^{n+1}(L_\lambda^{(2)} - L_\Lambda^{(1)}) f_{1,n}(R + \lambda_A) f_{2,n}(R + \lambda_A)}{L_n(\lambda_A, \lambda_A)}, \tag{D.13}
\]

where

\[
L_n(\lambda_A, \lambda_A) = \frac{F_1(R)}{F_2(R + \lambda_A)} \left( \frac{f_{1}(R + \lambda_A) f_{2}^{(2)}(L_\lambda^{(2)} - L_\Lambda^{(1)})}{f_{1}(R + \lambda_A) f_{2}(R + \lambda_A)} - \frac{f_{2}(R + \lambda_A) f_{1}^{(1)}(L_\lambda^{(2)} - L_\Lambda^{(2)})}{f_{2}(R + \lambda_A)} \right) - \frac{F_2(R)}{F_2(R + \lambda_A)} \left( \frac{f_{1}(R + \lambda_A) f_{2}^{(2)}(L_\lambda^{(1)} - L_\Lambda^{(2)})}{f_{1}(R + \lambda_A) f_{2}(R + \lambda_A)} - \frac{f_{2}(R + \lambda_A) f_{1}^{(1)}(L_\lambda^{(1)} - L_\Lambda^{(2)})}{f_{2}(R + \lambda_A)} \right), \tag{D.14}
\]

while \( f_{1,i}^{(k)} \), \( f_{2,i}^{(k)} \), and \( L_i^{(k)} \) \((i = 1, 2)\) are given as the logarithmic derivatives of the expressions in equation (D.12) ;
\[ P^{(i)} = \frac{n + 1}{R(1 + Q_n)} + \frac{d}{dr} \ln(f_{i,n}(r)) \bigg|_{r=R+\Lambda} \]  
\[ L^{(i)} = \frac{n + 1}{R(1 + Q_n)} + \frac{d}{dr} \ln(f_{i,n}(r)) \bigg|_{r=R+\Lambda} \]

\[ \Lambda = n_{\Lambda} \text{ (while } n + n + n, \text{ and } n + n, \text{ is fixed). The coefficients } a_{12} \text{ in the limit analytic part, diverging } \]

\[ \text{approximate expressions for } q \text{ (independent of } q \text{ and the analytic part into a Taylor series in powers of } q \). This leads to the following approximate expressions for } C_{n=1}^{(k)}: \]

\[ C_1^{(1)} = \frac{2(\Delta \varepsilon_1)^2}{R q_\lambda} \exp \left( \frac{\phi_m^2}{q \lambda} \right) \left( 1 - [e^{-\varepsilon_m^4}((\varepsilon_1 \Delta \varepsilon_1 - \varepsilon_m^4) - 3(\varepsilon_1 - 1)\Delta \varepsilon_1 + 2\varepsilon_m^4} \right. \]

\[ + 2e^4 (\Delta \varepsilon_1 + \varepsilon_1 \Delta \varepsilon_1 - \varepsilon_m^4) - (\varepsilon_1 - 2)\varepsilon_m^4 \Delta \varepsilon_1 = \]  
\[ \frac{q_\lambda}{\varepsilon_m^4 \Delta \varepsilon_1} \right) \cup \cup \]

\[ C_1^{(2)} = \frac{\Delta \varepsilon_1}{3 R q_\lambda} \left( 1 - \frac{2(e^4 - 1)}{\Delta \varepsilon_1} \right) \]

\[ C_1^{(3)} = -\frac{\Delta \varepsilon_1}{R q_\lambda (\varepsilon_m - 1)} \left( 1 - \frac{2(e^4 (\varepsilon_m^4 + \varepsilon_1 \Delta \varepsilon_1 - \varepsilon_m^4) - (\varepsilon_1 - 1)\Delta \varepsilon_1 \Delta \varepsilon_1)}{\varepsilon_m^4 \Delta \varepsilon_1} q_\lambda \right) \]

\[ C_1^{(4)} = -\frac{\Delta \varepsilon_1}{3 R q_\lambda (1 - \varepsilon_m^4) \left( (\varepsilon_m - 1) q_\lambda \right)} \exp \left( \frac{(1 + q_\lambda \varepsilon_m^4) e_m^4}{(\varepsilon_m - 1) q_\lambda} \right) \]

\[ \times \left( 1 + \frac{(\varepsilon_m^4 + \varepsilon_1 \Delta \varepsilon_1 - 1)\Delta \varepsilon_1 - 2e^4 (\varepsilon_m^4 + \varepsilon_1 \Delta \varepsilon_1 - \varepsilon_m^4)}{\varepsilon_m^4 \Delta \varepsilon_1} q_\lambda \right) \]

\[ C_1^{(5)} = 1 + \frac{2(\varepsilon_m^4 + \varepsilon_1 \Delta \varepsilon_1 - 1)\Delta \varepsilon_1 - e^4 (\varepsilon_m^4 + \varepsilon_1 \Delta \varepsilon_1 - \varepsilon_m^4)}{\varepsilon_m^4 \Delta \varepsilon_1} q_\lambda. \]
Since \( g'(r = R) \) is given by

\[
g'(R) = \left( \frac{d}{dr} g_1^2(r) \right)_{r=R} = C_{11}^1 F_1^1(r)_{r=R} + C_{12}^2 F_2^1(r)_{r=R},
\]

by using equations (D.16) and (D.17) we obtain the following approximation in the limit \( q_A \ll 1 \)

\[
g'(R) = -\frac{2e_A^\Delta}{R} + [e^{-e_A^\Delta} + 2e^{e_A^\Delta}](\varepsilon_m^A e^{\Delta e_A} + z_A \Delta e_A - \varepsilon_m^A) + ((z_A - 2)\varepsilon_m^A + 3(z_A - 1)) \Delta e_A) - \frac{2e_A^\Delta}{\varepsilon_m^A \Delta e_A R} q_A.
\]

The leading term in this expansion has been used in equation (88) in section 5. For \( \varepsilon_m^A = \varepsilon_w^A = 0 \) the sub-leading term vanishes.

### D.5. Force and velocity integrals

First we consider the integral \( I_A \) in equation (55). To this end we write \( I_A = I_A^- + I_A^+ \), where the first term and the second term result from integrations over the inner (repulsive) and the intermediate (attractive) regions of the pair potential, respectively. (The contribution due to the integration over the outer region vanishes because there \( W_2^\varepsilon(r) \equiv 0 \).

By using the above results, we find that in leading and sub-leading order in \( q_A \) the integral \( I_A^- \) is given by

\[
I_A^- = \int_{R}^{R+\lambda_A} dr \frac{e_A}{\varepsilon_m^A} \frac{W_{2}^\varepsilon(r)}{\varepsilon_m^A} g_2^2(r) \exp(-\beta W_1^\varepsilon(r))\]

\[
= -\frac{e_A^\Delta(e^{\Delta e_A} - 1)R^2}{\beta} \left(1 - \frac{2}{\Delta e_A} \left[1 + e_A^\Delta - \frac{\Delta e_A e^{\Delta e_A} (e^{\Delta e_A} + 1)}{e^{\Delta e_A} - 1}\right] q_A\right).
\]

The leading order term in equation (D.20) is negative for \( \Delta e_A > 0 \) and vanishes if \( \Delta e_A = 0 \) (i.e. if there is no interaction), and it is proportional to \( R^2 \). Similarly, in leading and sub-leading order in \( q_A \) the integral \( I_A^+ \) is given by

\[
I_A^+ = \int_{R}^{R+\lambda_A} dr \frac{e_A}{\varepsilon_m^A} \frac{W_{2}^\varepsilon(r)}{\varepsilon_m^A} g_2^2(r) \exp(-\beta W_1^\varepsilon(r))\]

\[
= \frac{(e^{-e_A^\Delta} - 1)R^2}{\beta} \left(1 - \frac{2}{e_A^\Delta \Delta e_A (e^{-e_A^\Delta} - 1)} \left[ e_A^\Delta e^{-e_A^\Delta} (e^{-e_A^\Delta} - 1) - (\varepsilon_m^A + z_A \Delta e_A) e^{e_A^\Delta} + \Delta e_A (z_A - 1 - e_A^\Delta) e^{-e_A^\Delta} + (2z_A - 1) \Delta e_A - 1\right] q_A\right).
\]

The leading term in this expression is positive for all \( \varepsilon_m^A \leq 0 \), and, as \( I_A^+ \), it is proportional to \( R^2 \).

It follows that the integral \( I_A \) is, in leading and sub-leading order in \( q_A \), given by

\[
I_A = -\frac{(1 - e^{-e_A^\Delta}) R^2}{\beta} - [(\varepsilon_A^A - z_A \Delta e_A) \sinh(e_A^A) - \varepsilon_m^A (\sinh(\varepsilon_m^A) - z_A \Delta e_A)] - \frac{4 \lambda_A R}{\beta e_A^\Delta \Delta e_A}.
\]
The leading order term in equation (D.22) is used in equation (87) in section 5. It depends only on $\varepsilon_m^A$, it is negative for $\varepsilon_m^A > 0$, and it is proportional to $R^2$. If $\varepsilon_m^A = 0$, the first term in equation (D.22) vanishes; in this case, in leading order in $q_A$ the force integral $I_A$ takes the form

$$I_A = z_A \left( \frac{\sinh(\varepsilon_m^A)}{\varepsilon_m^A} - 1 \right) \frac{4\lambda_A}{\beta} R,$$

which implies that it is positive and depends only linearly on $R$.

Next we consider the integral $J_A$ (equation (73)), which enters into the definition of the velocity $V$ (equations (72) and (75)) and of the stall force $F_{ex}$ (equations (79) and (80)). As for the integral $I_A$, we write $J_A = J_A^c + J_A^c$ (the contribution from the outer region vanishes in this case, too), where

$$J_A^c = \int_{R}^{R+\lambda_A} dr \, \frac{r}{r} \frac{W_A^c(r)}{d r} \left( 1 + \frac{1}{2} \left( \frac{R}{r} \right)^3 - \frac{3}{2} \frac{R}{r} \right) \exp(-\beta W_A^c(r))$$

$$= \frac{3}{2(\varepsilon_m^A)^2} \left( \lambda_A^2 \frac{\beta}{\varepsilon_m^A} - 2(z_A - 1)\varepsilon_m^A + 2(\varepsilon_m^A - 1)^2 \right) \left( \frac{\lambda_A^2}{\beta} \right)$$

$$\Delta \varepsilon_A \left( 6 - \Delta \varepsilon_A(6 - \Delta \varepsilon_A) - 6 \right) \frac{\lambda_A^2}{2(\Delta \varepsilon_A)^2} q_A,$$

and

$$J_A^c = \int_{R+\lambda_A}^{R+2\lambda_A} dr \, \frac{r}{r} \frac{W_A^c(r)}{d r} \left( 1 + \frac{1}{2} \left( \frac{R}{r} \right)^3 - \frac{3}{2} \frac{R}{r} \right) \exp(-\beta W_A^c(r))$$

One finds that for any $\Delta \varepsilon_A > 0$ the leading order term in $J_A^c$ is negative (similarly to the behavior exhibited by $I_A$ (equation (D.20))), and is independent of $R$. Equations (D.24) and (D.25) lead to

$$J_A = \frac{\lambda_A^2}{\beta} + S_A \frac{\lambda_A^2}{2\beta} q_A.$$

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The contribution from the leading term $J_λ(λA)^2β$ (see equation (102)) is used in equation (101) in section 5. The sub-leading contribution $S_λ$ in equation (D.26) collects all terms in square brackets in equations (D.24) and (D.25).

**D.6. Asymptotic behavior of $f_{de}(θ_0)$ in the limit $q_A → 0$**

Finally we consider the asymptotic behavior of the steric factor $f_{de}(θ_0)$ in the limit $q_A → 0$. According to equation (31) this amounts to the analysis of the behavior of the ratio $g_n'(R)/g_0'(R)$.

This behavior contains the following subtle issue. Due to equations (D.11) and (D.12), the radial functions $g_n(r)$ are defined explicitly via Kummer’s and Tricomi’s hypergeometric functions $M(\cdot)$ and $U(\cdot)$. In the limit $q_A → 0$ the arguments of both functions become large, which facilitates the derivation of the asymptotic behavior. On the other hand, the sub-dominant terms in the expansions of these hypergeometric functions for large arguments also depend on whether the parameters of the hypergeometric function are fixed and finite, or are allowed to vary and become large. Accordingly, the calculation of the correction terms to the leading order behavior poses a mathematically very involved problem. We therefore focus only on the leading order behavior of $g_n'(r = R)$ (with $g_n(r)$ defined by equations (D.11) and (D.12)):

$$g_n'(R) = C_n^{(1)} F_{1,n}'(r)_{r\to R} + C_n^{(2)} F_{2,n}'(r)_{r\to R}. \tag{D.27}$$

In the limit $q_A \ll 1$, the leading order behavior of the terms in equation (D.27) is

$$C_n^{(1)} \sim \frac{(n + 1)\Delta ε_A}{q_A} \left( \frac{\Delta ε_A}{q_A R} \right)^n \exp \left( \frac{ε_A^d + \Delta ε_A}{q_A} \right),$$

$$F_{1,n}'(R) \sim -\frac{q_A}{R} \left( \frac{Rq_A}{\Delta ε_A} \right)^n \exp \left( -\frac{\Delta ε_A}{q_A} \right), \tag{D.28}$$

and

$$C_n^{(2)} \sim \frac{\Gamma(n + 1)\Delta ε_A}{\Gamma(2n + 2)} \left( \frac{\Delta ε_A}{q_A R} \right)^n,$$

$$F_{2,n}'(R) \sim (-1)^{n+1} \frac{\Gamma(2n + 2)q_A}{\Gamma(n)\Delta ε_A} \left( \frac{q_A R}{\Delta ε_A} \right)^n \exp \left( -\frac{\Delta ε_A}{q_A} \right). \tag{D.29}$$

These expressions imply that the first term in equation (D.27) provides the dominant contribution, which is independent of $q_A$, while the second term is proportional to $q_A$. Therefore one finds for the leading behavior

$$g_n'(R) \sim -\frac{(n + 1)}{R} e^{ε_A}, \tag{D.30}$$

which is consistent with equations (D.10) and (D.19) and implies $g_n'(R)/g_0'(R) \sim (n + 1)$, so that $f_{de}(θ_0) \sim f_{de}'(θ_0)$ (see equation (33)).
Appendix E. Notations and definitions

$A, B, C$ (near figure 1): reactant and product molecular species;
$D_j$ (beginning of section 2), $j = A, B, C$: diffusion constant of the molecules of species $j$;
$F_{\text{chem}}, F_{\text{hyd}}$ (equation (54), after equation (53)): contributions to the force on the colloid due to the direct interactions with the molecules of various species and due to the flow of the solution, respectively;
$F_{\text{ext}}$ (equations (53), (77)–(80)): external force acting on the colloid; stall force, if it corresponds to $V = 0$;
$F_{\text{ext}}, V_j, j = A, B, C$ (equations (104), (105)): that part of the stall force and of the velocity, respectively, which is due to the species $j$;
$I_{p, j} = A, B, C$ (equation equations (55), (61)): force integrals in the definition of $F_{\text{chem}}$;
$I_{j} = A, B, C$ (equations (73)–(76)): velocity integrals in the definition of $V$;
$J_{j}, j = A, B, C$ (equation (102)): dimensionless factor in the velocity integral $J_j$ for species $j$;
$J$ and $J_{j}, j = A, B, C$ (see appendix A): particle current in the laboratory frame and relative to the (local) center of mass motion, respectively;
$K = W_0 V_0$ (after equation (9)): total number of reaction events per unit time (rate of reaction $W_0$) in a volume $V_0$;
$K_{\text{eff}}$ (equation (26)): effective reaction rate;
$K_{\text{eff}}$ (equation (32)): effective reaction rate in the absence of interactions between molecules and the colloid;
$K_S$ (after equation (27)): Schmoluchowski constant;
$K^*$ (equation (30)): effective reaction rate for an elementary reaction act;
$K_{\text{SD}}$ (equation (29)): Schmoluchowski-Debye constant;
$L_{ij}, i, j = A, B, C$ (equation (A.10)): Onsager coefficients;
$P$ (equations (48)): hydrostatic pressure (the isotropic part of the stress tensor);
$P_e, Re$ (near equations (A.14) and (48)): Péclet and Reynolds numbers, respectively;
$Q$ (equations (11) and (13)): constant negative particle current over the catalytic patch;
$R$ (figure 1): radius of the colloid;
$R_D$ (equation (17)): Debye radius;
$S$: solvent molecular species;
$T$: absolute temperature;
$V, V = |V|$: velocity of the colloid and its magnitude, respectively;
$V$: volume of the system;
$W_{j} = \Phi_{j}(r) - \frac{m_j}{m_a} \Phi_{a}(r), j = A, B, C$ (equation (3)): effective (relative to the solvent) interaction potential of molecules of type $j$ with the colloid;

$a$ (near equation (1)): minimal distance between a molecule of species $A$ and the colloid surface;
$a_{n}, b_{n}, \gamma_{n}$ (equations (27), (45) and (B.4)): coefficients in the series expansion of the radial functions of integer index $n \geq 0$ describing the dependence on $r$ of the number densities $n_A$, $n_B$, and $n_C$, respectively;
$c_{j}, j = A, B, C$: concentration (mass fraction) of molecular species $j$;
$f_{g}$ (equation (9)): geometric steric factor;
$f_{dc}$ (equation (31)): effective (diffusion-controlled) steric factor;
$f_{dc}^{\text{sls}}$ (equation (33)): effective steric factor in the absence of interactions between molecules and the colloid;
\( \mathbf{f} \) (equation (48)): force density on the fluid with (tilde) or without the contribution due to the gradient of the interactions between the solvent molecules and the colloid, respectively; 
\( g_n, j_n, h_n \) (equations (14), (43), (B.2)): radial functions of integer index \( n \geq 0 \) describing the dependence on \( r \) of the number densities \( n_A, n_B, \) and \( n_C \), respectively; 
\( k_B \): Boltzmann constant; 
\( m_j, j = A, B, C, S \) (near figure 1): molecular mass of species \( j \); 
\( n_j \) (near equation (1)), \( j = A, B, C \): number density of molecular species \( j \); 
\( n_0 \) (near equation (1)): bulk value of the number density of species \( A \); 
\( n_0^{(S)} \) (near equation (1)): mean number density of solvent molecules; 
\( p \) (equation (1)): probability of the conversion \( A \leftrightarrow B \); 
\( q_j, Q_j, z_j \) (after equation (86)): dimensionless parameters of the triangular-well potential for species \( j \); 
\( r, r = |\mathbf{r}| \) (figure 1): position vector and radial coordinate measured from the center of the colloid, respectively; 
\( \tilde{r} = r - R \) (figure 1): distance from the surface of the colloid; 
\( \mathbf{u}(\mathbf{r}) \) (near equation (48)): hydrodynamic flow of the solution; 
\( \hat{\Pi} \) (equations (48), (49)): Newtonian fluid stress tensor; 
\( \hat{\Phi}(\tilde{r}) \) and \( \Phi(r) = \hat{\Phi}(r - R) \), \( j = A, B, C, S \) (near equation (3)): interaction potential between a molecule of species \( j \) and the colloid; 
\( \Omega_{AB}^{(ij)} \) (equation (57)), \( \Omega_{ABC}^{(ij)} \) (equation (63)): contribution to parts in the force integrals which are independent of \( \theta_0 \); 
\( \beta = 1/(k_B T) \) (after equation (3)); 
\( \delta V \) (see appendix A): small volume element in the solution; 
\( \theta_0 \) (figure 1): opening polar angle (in spherical coordinates) of the catalytic patch; 
\( \theta \) (figure 1): polar angle in spherical coordinates; 
\( \kappa \) (equations (9), (10)): effective velocity defining the particle currents due to reactions at the catalytic patch; 
\( \mu \): viscosity of solution; 
\( \mu_j \) and \( \tilde{\mu}_j = \mu_j + \Phi_j, j = A, B, C, S \) (equation (A.4)): chemical potential of molecular species \( j \); 
\( \tilde{\mu}_j = (\mu_j/m_j) - (\mu_S/m_S) \), \( j = A, B, C \) (equation (A.12)): chemical potential relative to that of the solvent; 
\( \beta_j = [(\tilde{\mu}_j/m_j) - (\tilde{\mu}_S/m_S)]\rho, j = A, B, C \) (equation (A.7)): chemical potential of the molecular species \( j \) relative to that of solvent molecules, including the contribution from the interactions with the colloid; 
\( \xi_{1,2}, \lambda_j, \lambda_j, \Delta \epsilon, \epsilon_n^j, \epsilon_{in}^j \) \( j = A, B, C \) (equations (81)–(86)): parameters of the triangular-well potential for species \( j \); 
\( \rho \) (equation (A.1)): mass density of the solution; 
\( \sigma_j, \epsilon_j \), \( j = A, B, C, S \) (after equation (3)): parameters of the Lennard-Jones pair potential between molecules of species \( j \) and molecules composing the colloid; 

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