

Fluctuating chemohydrodynamics and the stochastic motion of self-diffusiophoretic particles

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The propulsion of active particles by self-diffusiophoresis is driven by asymmetric catalytic reactions on the particle surface that generate a mechanochemical coupling between the fluid velocity and the concentration fields of fuel and product in the surrounding solution. Because of thermal and molecular fluctuations in the solution, the motion of micrometric or submicrometric active particles is stochastic. Coupled Langevin equations describing the translation, rotation, and reaction of such active particles are deduced from fluctuating chemohydrodynamics and fluctuating boundary conditions at the interface between the fluid and the particle. These equations are consistent with microreversibility and the Onsager-Casimir reciprocal relations between affinities and currents and provide a thermodynamically consistent basis for the investigation of the dynamics of active particles propelled by diffusiophoretic mechanisms. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5020442>

I. INTRODUCTION

Nature often makes use of molecular machines that convert chemical energy supplied by their environments into directed motion that is then exploited to carry out various transport and other biological functions.¹ One need not rely on nature to construct small machines, and synthetic self-propelled nano- and micro-motors use catalytic chemical reactions on a portion of the motor to achieve directed motion. Such motors have been made and are the focus of much interest because of the myriad of potential applications that make use of their small size and ability to carry out active transport.^{2–8} These active particles are driven by gradients of concentrations, electrochemical potentials, or temperature generated by the surface reactions and operate in nonequilibrium systems where energy transduction from reaction to motion is induced by mechanochemical coupling through diffusiophoresis, electrophoresis, or thermophoresis.^{9–11}

Because of their micrometric or submicrometric sizes, active particles are subjected to thermal and molecular fluctuations in the solution, in which they reside, so that a stochastic description of the system is required to study their dynamics. In this regard, a challenging issue is how to bridge the gap between the fluctuating chemohydrodynamics describing the fluid and the stochastic movements of the active particle while remaining consistent with the principles of nonequilibrium thermodynamics.^{12–17}

The purpose of the present paper is to address this issue and set up a framework to deduce overdamped Langevin

equations ruling the stochastic translation, rotation, and reaction of an active particle self-propelled by diffusiophoresis, starting from a fluctuating continuous-medium description. The key element in this analysis is the need to understand the interplay between the boundary conditions for the fluid velocity and solute concentration fields at the interface with the active particle. The boundary conditions express the coupling between the interfacial processes generating the mechanochemical coupling. These processes are the surface reaction, the diffusiophoretic effect, and the interfacial friction due to slip velocity. To be consistent with microreversibility, the linear response coefficients describing these interfacial processes must satisfy the Onsager-Casimir reciprocal relations.^{18–22} Since the mechanochemical coupling is generated by diffusiophoresis, there exists a reciprocal effect back onto the concentration fields and the reaction, which has consequences for the coupled stochastic equations ruling the motion and reaction of the particle. Because of this reciprocal effect, the reaction rate depends on the mechanical force exerted on the particle. The inclusion of this reciprocal effect is essential in order to obtain the mechanochemical fluctuation theorem that governs the stochastic motion of the chemically propelled motor.²³

The plan of this paper is the following. In Sec. II, the fluctuating chemohydrodynamics formulation is presented for a solution containing a Janus particle with a catalytic surface where an interfacial reaction takes place. The frequency-dependent force, torque, and reaction rate of the particle are deduced from these boundary conditions in Sec. III. In Sec. IV, the low-frequency limit is considered in order to obtain analytical expressions for these quantities for a spherical Janus particle composed of catalytic and noncatalytic hemispheres. In this way, the diffusiophoretic force is expressed in terms of diffusiophoretic constants and the reaction rate. In Sec. V,

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the coupled overdamped Langevin equations, as well as the associated Fokker-Planck equation, are deduced for the stochastic motion and reaction of the Janus motor and their implications are studied. The conclusions are given in Sec. VI, which summarizes the results and presents a perspective on the work.

II. FLUCTUATING CHEMOHYDRODYNAMICS WITH SURFACE REACTIONS

Fluctuating thermodynamics methods are well known and provide a way to incorporate thermal fluctuations in continuum descriptions of the dynamics.^{24–27} In the linear regime, close to thermodynamic equilibrium, the fluctuation-dissipation theorem provides a systematic method to set up the stochastic differential equations describing the random motion of the variables that are used to describe the dynamics of the system. To implement this scheme, the different irreversible processes $\{\alpha\}$ are identified and the thermodynamic entropy production rate is written as a linear combination of products of their affinities $\{A_\alpha\}$ and noiseless currents $\{\langle J_\alpha \rangle\}$,^{12–17}

$$\frac{1}{k_B} \frac{d_i S}{dt} = \sum_\alpha A_\alpha \langle J_\alpha \rangle \geq 0, \quad (1)$$

where k_B is Boltzmann's constant and $\langle \cdot \rangle$ denotes the statistical average over the fluctuations. The non-negativity of the entropy production rate is the expression of the second law of thermodynamics, implying that the entropy of an isolated system increases up to a maximum reached at equilibrium. Phenomenological linear relations are established between the currents and the affinities

$$\langle J_\alpha \rangle = \sum_\beta L_{\alpha\beta} A_\beta \quad (2)$$

in terms of linear response coefficients $L_{\alpha\beta}$ so that the entropy production rate takes the quadratic form

$$\frac{1}{k_B} \frac{d_i S}{dt} = \sum_{\alpha,\beta} L_{\alpha\beta} A_\alpha A_\beta \geq 0. \quad (3)$$

As a consequence of microreversibility, the linear response coefficients obey the Onsager-Casimir reciprocal relations $L_{\alpha\beta} = \epsilon_\alpha \epsilon_\beta L_{\beta\alpha}$, where $\epsilon_\alpha = \pm 1$ when A_α is even or odd under time reversal.^{16–22} Accordingly, only the coefficients $L_{\alpha\beta}$ that couple processes with the same parity under time reversal contribute to the entropy production rate (3).

Fluctuating currents are obtained by adding a noise term $\delta J_\alpha(t)$ to the mean currents,

$$J_\alpha = \sum_\beta L_{\alpha\beta} A_\beta + \delta J_\alpha(t). \quad (4)$$

By virtue of the fluctuation-dissipation theorem holding close to equilibrium, and since the system has many degrees of freedom, the fluctuating quantities $\delta J_\alpha(t)$ are assumed to be Gaussian white noise processes characterized by

$$\begin{aligned} \langle \delta J_\alpha(t) \rangle &= 0 \quad \text{and} \\ \langle \delta J_\alpha(t) \delta J_\beta(t') \rangle &= (L_{\alpha\beta} + L_{\beta\alpha}) \delta(t - t'), \end{aligned} \quad (5)$$

on time scales longer than correlation times.^{24–27} We note that Eq. (5) vanishes if processes with opposite parities under

time reversal are coupled together by coefficients such that $L_{\alpha\beta} = -L_{\beta\alpha}$, in which case there is no associated noise to consider.

Making the assumption of local thermodynamic equilibrium, the same principles may be used to construct the stochastic equations for spatially extended systems.^{25–28}

The general stochastic thermodynamics method outlined above will now be applied to describe Janus motors propelled by a diffusiophoretic mechanism. A Janus motor is a spherical particle with catalytic and noncatalytic hemispheres, and we suppose that it is suspended in a multi-component fluid containing solute species, labeled by the index k , that interact with the motor through short range intermolecular potentials u_k . We further assume that the reversible reactions $A \rightleftharpoons B$ occur on the catalytic hemisphere and call species A the fuel and B the product. These chemical reactions produce inhomogeneous c_A and c_B concentration fields in the motor vicinity that lead to a body force on the motor. If no external forces act on the system and momentum is conserved, fluid flows arise in the surrounding medium which are responsible for motor propulsion. The forms that the stochastic equations for the fluid velocity and concentration fields take in the solution and on the surface are given below.

A. Stochastic equations in the bulk phases

If the exothermicity of the reaction is negligible, we may suppose that the system remains isothermal with an invariant and uniform temperature T . The hydrodynamic and diffusive processes in the solution surrounding the catalytic Janus particle are described by the coupled Navier-Stokes and diffusion equations. The fluctuating Navier-Stokes equation ruling the velocity field $\mathbf{v}$ is given by

$$\rho (\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) = -\text{div } \mathbf{P}, \quad (6)$$

where ρ is the mass density and $\mathbf{P}$ is the pressure tensor.^{25–28} The fluid is assumed to be incompressible,

$$\nabla \cdot \mathbf{v} = 0, \quad (7)$$

so that the mass density remains uniform. In this case, the pressure tensor is related to the gradients of the velocity field by the phenomenological linear relations,

$$P_{ij} = P \delta_{ij} - \eta (\partial_i v_j + \partial_j v_i) + \pi_{ij}, \quad (8)$$

where P is the hydrostatic pressure, η is the shear viscosity, and π_{ij} are Gaussian white noise fields characterized by

$$\begin{aligned} \langle \pi_{ij}(\mathbf{r}, t) \rangle &= 0 \quad \text{and} \\ \langle \pi_{ij}(\mathbf{r}, t) \pi_{kl}(\mathbf{r}', t') \rangle &= 2k_B T \eta (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \end{aligned} \quad (9)$$

in accord with the general relations given in Eqs. (4) and (5), where the current corresponds to the viscous part of the pressure tensor and the affinity to the gradient of the velocity field.^{25–28}

The fluctuating diffusion equations for the concentration fields c_k of the different solute species $k = 1, 2, \dots, s$ have the form

$$\partial_t c_k + \nabla \cdot \mathbf{j}_k = 0. \quad (10)$$

In a dilute solution where cross-diffusion is negligible, the fluctuating current densities can be expressed as

$$\mathbf{j}_k = c_k \mathbf{v} - D_k \nabla c_k + \boldsymbol{\eta}_k, \quad (11)$$

in terms of the molecular diffusivity D_k of species k and Gaussian white noise fields $\boldsymbol{\eta}_k$ satisfying^{26,27}

$$\begin{aligned} \langle \boldsymbol{\eta}_k(\mathbf{r}, t) \rangle &= 0 \quad \text{and} \\ \langle \boldsymbol{\eta}_k(\mathbf{r}, t) \boldsymbol{\eta}_{k'}(\mathbf{r}', t') \rangle &= 2D_k c_k \delta_{kk'} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \mathbf{1}, \end{aligned} \quad (12)$$

with $\mathbf{1}$ denoting the 3×3 identity matrix. With respect to Eqs. (4) and (5), here the currents correspond to the diffusive part of current densities and the affinities correspond to the gradients of chemical potentials $\mu_k = \mu_k^0 + k_B T \ln(c_k/c^0)$.¹⁷ Moreover, the noise terms on the pressure and current densities are uncorrelated, $\langle \pi_{ij}(\mathbf{r}, t) \boldsymbol{\eta}_{k'}(\mathbf{r}', t') \rangle = 0$.

Inside a solid Janus particle of radius R , the velocity and concentration fields take the following values:²⁹

$$\mathbf{v}(\mathbf{r}, t) = \mathbf{V}(t) + \boldsymbol{\Omega}(t) \times [\mathbf{r} - \mathbf{R}(t)] \quad \text{and} \quad c_k(\mathbf{r}, t) = 0, \quad (13)$$

for $\|\mathbf{r} - \mathbf{R}(t)\| < R$ and $k = 1, 2, \dots, s$, where $\mathbf{R}(t)$ is the position of the center of mass of the Janus particle, $\mathbf{V}(t)$ is its velocity, and $\boldsymbol{\Omega}(t)$ is its angular velocity.

B. Stochastic equations at the interface

Several processes take place at the interface between the fluid and the Janus particle. First, there is a frictional force along the interface associated with the partial slip of the velocity field between the fluid and the solid particle. Second, the reaction $A \rightleftharpoons B$ takes place on the catalytic hemisphere of the Janus particle with local rate,

$$w = \kappa_+ c_A - \kappa_- c_B, \quad (14)$$

where $\kappa_{\pm}$ are rate coefficients. Third, a diffusiophoretic force is exerted by the diffusing species on the Janus particle. All these processes can be described by boundary conditions on the velocity and concentration fields by extending interface nonequilibrium thermodynamics^{21,22,30,31} to stochastic processes.³² These boundary conditions take account of transport between the bulk of the solution and the interface with the solid particle.

The transport properties that are tangential to the interface are determined as in Ref. 22 using the expression for the interfacial thermodynamic entropy production to identify the interfacial currents and affinities. Here, the relevant currents are the tangential components of the pressure tensor $\mathbf{P}$ and the surface current density $\mathbf{j}_k^s$ of species k . The corresponding affinities, respectively, are proportional to the slip velocity $\mathbf{v}_{\text{slip}}$ between the fluid and the solid, and the tangential gradient $\nabla_{\perp}$ of the surface chemical potential μ_k^s of species k . According to Eqs. (4) and (5), we expect there to be a coupling between them as follows:

$$\mathbf{n} \cdot \mathbf{P} \cdot \mathbf{1}_{\perp} = -\frac{L_{vv}}{T} \mathbf{v}_{\text{slip}} - \sum_k \frac{L_{vk}}{T} \nabla_{\perp} \mu_k^s + \mathbf{f}_{\Pi}^s, \quad (15)$$

$$\mathbf{j}_k^s = -\frac{L_{kv}}{T} \mathbf{v}_{\text{slip}} - \sum_l \frac{L_{kl}}{T} \nabla_{\perp} \mu_l^s + \boldsymbol{\eta}_k^s, \quad (16)$$

where $\mathbf{n}$ denotes a unit vector normal to the interface and oriented toward the fluid, and $\mathbf{1}_{\perp} \equiv \mathbf{1} - \mathbf{n}\mathbf{n}$.

In Eq. (15), the quantity $\lambda = L_{vv}/T$ is the coefficient of sliding friction.³³ The fluctuating force per unit area associated with sliding friction, $\mathbf{f}_{\Pi}^s(\mathbf{r}, t)$, is discussed in Ref. 32 and is given by the Gaussian white noise process satisfying

$$\begin{aligned} \langle \mathbf{f}_{\Pi}^s(\mathbf{r}, t) \rangle &= 0 \quad \text{and} \\ \delta^s(\mathbf{r}, t) \langle \mathbf{f}_{\Pi}^s(\mathbf{r}, t) \mathbf{f}_{\Pi}^s(\mathbf{r}', t') \rangle \delta^s(\mathbf{r}', t') \\ &= 2k_B T \lambda \delta^s(\mathbf{r}, t) \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \mathbf{1}_{\perp}, \end{aligned} \quad (17)$$

where $\delta^s(\mathbf{r}, t)$ is the interfacial Dirac distribution.²²

In Eq. (16), the coefficients L_{kl} characterize diffusive transport tangential to the interface. If surface cross-diffusion were neglected, these coefficients would be related to the surface diffusion coefficients D_k^s . Indeed, in the presence of adsorbates with excess surface density Γ_k for species k , the second term on the right-hand side of Eq. (16) would read $-D_k^s \nabla_{\perp} \Gamma_k$ in agreement with Fick's law for surface diffusion, if $L_{kl}/T = \delta_{kl} D_k^s \Gamma_k / (k_B T)$. In this case, the interfacial Gaussian white noise terms $\boldsymbol{\eta}_k^s$ associated with surface diffusion would satisfy relations similar to Eqs. (17), but with $D_k^s \Gamma_k$ in place of $k_B T \lambda$.

Diffusiophoresis is characterized by the coefficients L_{vk} in Eq. (15). If there is local equilibrium between the species k at the interface and in the solution because transport is faster in the normal direction than in the tangential one, the surface and bulk chemical potentials should be equal, $\mu_k^s = \mu_k$, and both are determined by the bulk concentration c_k . Accordingly, we deduce from Eq. (15) the following boundary condition on the tangential component of the velocity field,

$$\begin{aligned} \mathbf{v}_{\text{slip}} &\equiv \mathbf{1}_{\perp} \cdot \{\mathbf{v}(\mathbf{r}, t) - \mathbf{V}(t) - \boldsymbol{\Omega}(t) \times [\mathbf{r} - \mathbf{R}(t)]\} \\ &= \mathbf{1}_{\perp} \cdot \left\{ b \left[\nabla \mathbf{v}(\mathbf{r}, t) + \nabla \mathbf{v}(\mathbf{r}, t)^T \right] \cdot \mathbf{n} + \mathbf{f}_{\Pi}^s(\mathbf{r}, t) / \lambda \right. \\ &\quad \left. - \sum_k b_k \nabla c_k(\mathbf{r}, t) \right\} \end{aligned} \quad (18)$$

for $\|\mathbf{r} - \mathbf{R}(t)\| = R$. Here, $b = \eta/\lambda$ is the slip length, and the b_k are the diffusiophoretic constants,

$$b_k \equiv k_B \frac{L_{vk}}{\lambda c_k} = \frac{k_B T}{\eta} \left(K_k^{(1)} + b K_k^{(0)} \right), \quad (19)$$

which are given in terms of the quantities,

$$K_k^{(n)} \equiv \int_R^{R+\delta} dr (r - R)^n \left[e^{-\beta u_k(r)} - 1 \right], \quad (20)$$

where δ is the finite range of the intermolecular potentials $u_k(r)$ in the direction r that is radial from the center of mass of the Janus particle, and $\beta = (k_B T)^{-1}$.³⁴⁻³⁷ The expression (18) for the slip velocity that includes the diffusiophoretic term with the constants (19) in the presence of partial slip was obtained

previously.³⁷ Here we assume that the reaction has a negligible effect on the diffusiophoretic constants. In addition to the boundary condition (18), the normal component of the velocity field obeys³⁸

$$\mathbf{n} \cdot \mathbf{v}(\mathbf{r}, t) = \mathbf{n} \cdot \mathbf{V}(t) \quad (21)$$

for $\|\mathbf{r} - \mathbf{R}(t)\| = R$.

In order to satisfy microreversibility, the linear response coefficients in Eqs. (15) and (16) must obey the Onsager-Casimir reciprocal relations,

$$L_{kv} = -L_{vk} \quad \text{and} \quad L_{kl} = L_{lk}, \quad (22)$$

because $\mathbf{v}_{\text{slip}}$ is odd under time reversal, while $\nabla_{\perp} \mu_l^s$ is even. The relations in the first equality show that diffusiophoresis has a reciprocal effect back onto the surface current density (16), but there is no noise associated with diffusiophoresis as a consequence of Eq. (5).

The boundary conditions on the concentration fields are determined by the transport of the species in the direction normal to the interface, the surface reaction rate (14), and the reciprocal effect of diffusiophoresis. For species k , the boundary condition can be expressed as

$$\mathbf{n} \cdot (c_k \mathbf{v} - D_k \nabla c_k)_R = \nu_k(w + \xi^s) - \Sigma_k^s, \quad (23)$$

where ν_k is the stoichiometric coefficient, which is positive for the product, $\nu_B = 1$, and negative for the reactant, $\nu_A = -1$, and $\xi^s(\mathbf{r}, t)$ is the interfacial noise associated with the surface reaction (14) and satisfying

$$\begin{aligned} \langle \xi^s(\mathbf{r}, t) \rangle &= 0 \quad \text{and} \\ \delta^s(\mathbf{r}, t) \langle \xi^s(\mathbf{r}, t) \xi^s(\mathbf{r}', t') \rangle \delta^s(\mathbf{r}', t') \\ &= (\kappa_+ c_A + \kappa_- c_B) \delta^s(\mathbf{r}, t) \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'). \end{aligned} \quad (24)$$

Furthermore, there is a possible sink into the interface given by

$$\Sigma_k^s = \partial_t \Gamma_k + \nabla_{\perp} \cdot (\Gamma_k \mathbf{v}^s + \mathbf{j}_k^s), \quad (25)$$

where $\mathbf{v}^s$ is the surface velocity and $\mathbf{j}_k^s$ is the surface current density (16), which is determined, in particular, by the reciprocal effect of diffusiophoresis. This effect is a consequence of microreversibility and the Onsager-Casimir reciprocal relations in the coupling with the coefficients L_{kv} between interfacial solute transport and the slip velocity, in analogy with the cross effects related to thermal slip.^{21,22} If there is local equilibrium between the interface and the bulk of the solution, the excess surface density is driven by the corresponding concentration according to $\Gamma_k = K_k^{(0)} c_k(r = R)$ with the proportionality constant given by Eq. (20) for $n = 0$.^{35,36} Otherwise, the excess surface density Γ_k is an autonomous interfacial field ruled by Eq. (25).³¹

The boundary conditions (18), (21), and (23) will be used in Sec. III to determine the effects of the surrounding solution on the Janus motor.

III. FREQUENCY-DEPENDENT FORCE, TORQUE, AND REACTION RATE

The force exerted on the Janus particle by the fluid is determined by the surface integral of the pressure tensor at the

interface $\mathcal{S}(t)$ between the fluid and the Janus particle and, if present, an external force $\mathbf{F}_{\text{ext}}$. As a consequence, Newton's equation for the Janus particle is given by

$$m \frac{d\mathbf{V}}{dt} = - \int_{\mathcal{S}(t)} \mathbf{P}(\mathbf{r}, t) \cdot \mathbf{n} dS + \mathbf{F}_{\text{ext}}, \quad (26)$$

where $m = \int_{\mathcal{V}(t)} \rho_{\text{sol}} d\mathbf{r}$ is the mass of the Janus particle and ρ_{sol} is its mass density.^{28,29}

In a similar manner, a torque is exerted by the fluid on the Janus particle so that the angular velocity obeys the equation

$$\mathbf{I} \cdot \frac{d\boldsymbol{\Omega}}{dt} = - \int_{\mathcal{S}(t)} \Delta \mathbf{r} \times [\mathbf{P}(\mathbf{r}, t) \cdot \mathbf{n}] dS + \mathbf{T}_{\text{ext}}, \quad (27)$$

where the inertia tensor $\mathbf{I}$ of the Janus particle has the components $I_{ij} = \int_{\mathcal{V}(t)} \rho_{\text{sol}} (\Delta \mathbf{r}^2 \delta_{ij} - \Delta r_i \Delta r_j) d\mathbf{r}$ with $\Delta \mathbf{r} \equiv \mathbf{r} - \mathbf{R}(t)$, and $\mathbf{T}_{\text{ext}}$ is an external torque.^{32,39-41}

The overall reaction rate of the Janus particle is given by

$$W = \int_{\mathcal{S}(t)} dS (\kappa_+ c_A - \kappa_- c_B)_R, \quad (28)$$

where the surface integral is carried out over the catalytic hemisphere of the Janus particle because the rate constants $\kappa_{\pm}$ vanish on the noncatalytic hemisphere.

A. Linearization and induced force density

The aforementioned stochastic partial differential equations are nonlinear, and they are linearized in order to obtain their solutions.^{28,29} The linearization is justified if the Reynolds number

$$\text{Re} \equiv \frac{V_d R}{\nu} \ll 1 \quad (29)$$

so that the flow is laminar. Here V_d is the diffusiophoretic velocity of the Janus particle and $\nu = \eta/\rho$ is the kinematic viscosity. The condition (29) is well satisfied for micron-size Janus motors with typical velocities $V_d \sim 10^{-5}$ m/s in water solutions where $\nu \simeq 10^{-6}$ m²/s, since $\text{Re} \sim 10^{-5}$. In this low Reynolds number regime, the advective term $\mathbf{v} \cdot \nabla$ is negligible in comparison with the time derivative ∂_t , which is of order ν/R^2 .

Following Bedeaux and Mazur,²⁸ the problem is reformulated by introducing an induced force density field $\mathbf{f}_{\text{ind}}(\mathbf{r}, t)$ to represent the effects of the boundary conditions on the velocity field so that the linearized equation of motion of the fluid becomes

$$\rho \partial_t \mathbf{v}(\mathbf{r}, t) = -\text{div} \mathbf{P}(\mathbf{r}, t) + \mathbf{f}_{\text{ind}}(\mathbf{r}, t), \quad (30)$$

for an incompressible fluid where Eq. (7) holds, and with the pressure tensor given in Eq. (8). Taking the coordinate origin at the center of the Janus particle, the induced force density field is chosen to vanish in the fluid, $\mathbf{f}_{\text{ind}}(\mathbf{r}, t) = 0$ if $r > R$, and to comply with the constraints that the velocity field satisfies the linear equation $\mathbf{v}(\mathbf{r}, t) = \mathbf{V}(t) + \boldsymbol{\Omega}(t) \times \mathbf{r}$ if $r \leq R$, and the hydrostatic pressure is zero in the solid particle, $P(\mathbf{r}, t) = 0$ if $r < R$. As a consequence of Eq. (30), the induced force density in the solid particle is given by

$$\mathbf{f}_{\text{ind}}(\mathbf{r}, t) = \rho \frac{d}{dt} [\mathbf{V}(t) + \boldsymbol{\Omega}(t) \times \mathbf{r}] \quad \text{if } r < R, \quad (31)$$

but it is singular on the interface.²⁹

The linearized problem is solved by Fourier transformation in time,

$$\mathbf{v}(\mathbf{r}, \omega) = \int_{-\infty}^{+\infty} dt e^{i\omega t} \mathbf{v}(\mathbf{r}, t), \quad (32)$$

for the velocity and other fields so that Eq. (30), using Eqs. (7) and (8), becomes

$$(-i\omega\rho - \eta\nabla^2) \mathbf{v}(\mathbf{r}, \omega) = -\nabla P(\mathbf{r}, \omega) - \nabla \cdot \boldsymbol{\pi}(\mathbf{r}, \omega) + \mathbf{f}_{\text{ind}}(\mathbf{r}, \omega), \quad (33)$$

$$\nabla^2 P(\mathbf{r}, \omega) = -\nabla \nabla : \boldsymbol{\pi}(\mathbf{r}, \omega) + \nabla \cdot \mathbf{f}_{\text{ind}}(\mathbf{r}, \omega). \quad (34)$$

Introducing the Green function,

$$G(\mathbf{r}, \omega) = \frac{1}{4\pi\eta r} \exp(-\alpha r) \quad \text{with } \alpha = \sqrt{-i\omega/\nu} \quad (35)$$

(Re $\alpha \geq 0$), the solution of Eqs. (33) and (34) can be expressed as

$$\begin{aligned} \mathbf{v}(\mathbf{r}, \omega) = & \mathbf{v}_0(\mathbf{r}, \omega) + \int d\mathbf{r}' \left\{ G(\mathbf{r} - \mathbf{r}', \omega) + \frac{1}{\alpha^2} \frac{\partial}{\partial \mathbf{r}'} \frac{\partial}{\partial \mathbf{r}'} \right. \\ & \times [G(\mathbf{r} - \mathbf{r}', 0) - G(\mathbf{r} - \mathbf{r}', \omega)] \left. \right\} \cdot \mathbf{f}_{\text{ind}}(\mathbf{r}', \omega) \end{aligned} \quad (36)$$

in terms of the induced force density and the fluctuating velocity field $\mathbf{v}_0$ in the absence of the particle.^{28,29,38} The correlation functions of the Gaussian white noise velocity field $\mathbf{v}_0$ may be determined directly from Eq. (9). In the following, Eq. (36) is used to determine the force and the torque of the fluid on the particle.

B. Force of the fluid on the Janus particle

The fluctuating force exerted by the fluid on the Janus particle can be expressed in terms of the induced force density as²⁸

$$\begin{aligned} \mathbf{F}(\omega) = & - \int_S \mathbf{P}(\mathbf{r}, \omega) \cdot \mathbf{n} dS = - \int_{r \leq R} d\mathbf{r} \nabla \cdot \mathbf{P}(\mathbf{r}, \omega) \\ = & -i\omega\rho \frac{4\pi R^3}{3} \mathbf{V}(\omega) - \int_{r \leq R} d\mathbf{r} \mathbf{f}_{\text{ind}}(\mathbf{r}, \omega). \end{aligned} \quad (37)$$

The relation between the induced force density and the unperturbed velocity field $\mathbf{v}_0$ remains to be determined. For this purpose, the Fourier transforms of the boundary conditions (18) and (21) are averaged over the surface to obtain

$$\begin{aligned} \overline{\mathbf{1}_\perp \cdot \mathbf{v}(\mathbf{r}, \omega)}^s - b \overline{\mathbf{1}_\perp \cdot [\nabla \mathbf{v}(\mathbf{r}, \omega) + \nabla \mathbf{v}(\mathbf{r}, \omega)^T] \cdot \mathbf{n}}^s \\ + \overline{\mathbf{1}_\perp \cdot \mathbf{v}_\text{fl}^s(\mathbf{r}, \omega)}^s + \sum_k b_k \overline{\mathbf{1}_\perp \cdot \nabla c_k(\mathbf{r}, \omega)}^s = \frac{2}{3} \mathbf{V}(\omega), \end{aligned} \quad (38)$$

$$\overline{\mathbf{nn} \cdot \mathbf{v}(\mathbf{r}, \omega)}^s = \frac{1}{3} \mathbf{V}(\omega), \quad (39)$$

where

$$\overline{(\cdot)}^s = \frac{1}{4\pi R^2} \int_{r=R} (\cdot) dS. \quad (40)$$

In writing these equations, it has been assumed that the diffusiophoretic constants b_k take uniform values on the entire spherical surface of the particle, otherwise they should be included in the surface average on the left-hand side of Eq. (38). Using the identity $R \int_{r=R} \mathbf{nn} \cdot \mathbf{v} dS = \int_{r \leq R} \nabla \cdot \mathbf{v} d\mathbf{r}$, Eq. (39) can be written as the volume average of the velocity field,

$$\mathbf{V}(\omega) = \overline{\mathbf{v}(\mathbf{r}, \omega)}^v = \frac{3}{4\pi R^3} \int_{r \leq R} \mathbf{v}(\mathbf{r}, \omega) d\mathbf{r}. \quad (41)$$

From this point, the calculations in Sec. 3 of Ref. 38 can be followed step-by-step. Expression (36) for the velocity field is substituted in Eqs. (38) and (41) to get the volume integral of the induced force $\mathbf{f}_{\text{ind}}(\mathbf{r}, \omega)$ appearing on the right-hand side of Eq. (37). In this way, the force (37) is obtained in the form of a generalized Faxén theorem that includes contributions from diffusiophoresis. This force can be written as the sum of three terms,

$$\mathbf{F}(\omega) = -\gamma(\omega) \mathbf{V}(\omega) + \mathbf{F}_d(\omega) + \mathbf{F}_\text{fl}(\omega). \quad (42)$$

The first term is the frequency-dependent Stokes drag force $-\gamma(\omega) \mathbf{V}(\omega)$, where $\gamma(\omega)$ is the frequency-dependent Stokes friction coefficient,

$$\gamma(\omega) = 6\pi\eta R \left[\frac{(1 + \alpha R)(1 + 2b/R)}{1 + b(3 + \alpha R)/R} + \frac{\alpha^2 R^2}{9} \right]. \quad (43)$$

The second term is the frequency-dependent diffusiophoretic force,

$$\mathbf{F}_d(\omega) = \frac{6\pi\eta R (1 + \alpha R)}{1 + b(3 + \alpha R)/R} \sum_k b_k \overline{\mathbf{1}_\perp \cdot \nabla c_k(\mathbf{r}, \omega)}^s, \quad (44)$$

while the third term is the Langevin fluctuating force,

$$\begin{aligned} \mathbf{F}_\text{fl}(\omega) = & 6\pi\eta R \left\{ \frac{\alpha^2 R^2}{3} \overline{\mathbf{v}_0(\mathbf{r}, \omega)}^v + \frac{1 + \alpha R}{1 + b(3 + \alpha R)/R} \right. \\ & \times \left[1 + \frac{b}{R} \left(2 - R \frac{\partial}{\partial R} \right) \right] \overline{\mathbf{v}_0(\mathbf{r}, \omega)}^s \\ & \left. + \frac{1 + \alpha R}{1 + b(3 + \alpha R)/R} \overline{\mathbf{1}_\perp \cdot \mathbf{v}_\text{fl}^s(\mathbf{r}, \omega)}^s \right\}, \end{aligned} \quad (45)$$

which depends on the fluctuating unperturbed velocity field $\mathbf{v}_0(\mathbf{r}, \omega)$ and can be shown to obey the fluctuation-dissipation theorem,^{28,32}

$$\begin{aligned} \langle \mathbf{F}_\text{fl}(\omega) \rangle &= 0 \quad \text{and} \\ \langle \mathbf{F}_\text{fl}(\omega) \mathbf{F}_\text{fl}^*(\omega') \rangle &= 4\pi k_B T \text{Re } \gamma(\omega) \delta(\omega - \omega') \mathbf{1}. \end{aligned} \quad (46)$$

The expressions for the Stokes drag force and Langevin fluctuating force given above were obtained earlier.^{32,38} The frequency-dependent translational friction coefficient for stick boundary conditions is known⁴² and agrees with Eq. (43) for $b = 0$.

The equation of motion for a Brownian particle corresponding to the frequency-dependent friction has a memory kernel with a long-time tail and an extra acceleration term giving an effective mass $m + m_\text{fluid}/2$ where m_fluid is the mass of the displaced fluid.^{43–46} The long-time tail also manifests

itself in the time-dependent correlation function of the fluctuating force. In the noiseless limit, the equation of motion is consistent with that in Refs. 47 and 48. The effects of the long-time tail become negligible at low frequency if the Lorentz condition $m \gg m_{\text{fluid}}$ is satisfied, in which case the standard Langevin equation is recovered for a Brownian particle without the diffusiophoretic force.⁴⁴ A crossover to the Langevin low-frequency regime occurs for $|\alpha R| \sim 1$ around the frequency $\omega \sim \nu/R^2$ characteristic of shear viscosity. This low-frequency limit will be considered in Sec. IV.

If the compressibility of the fluid is taken into account, modifications appear beyond the frequency $\omega \simeq v_{\text{sound}}/R$ where v_{sound} is the sound velocity.⁴⁹ This is a very large frequency in the case of water where $\omega \simeq 1.5 \times 10^9 \text{ s}^{-1}$ so that these effects will be neglected here.

C. Torque of the fluid on the Janus particle

A Faxén-like theorem for the torque on a spherical particle using methods similar to those for the force was derived earlier.^{39–41} Extending such calculations to include the diffusiophoretic contribution, we find that the torque can also be written as the sum of three contributions,

$$\mathbf{T}(\omega) = -\gamma_r(\omega)\mathbf{\Omega}(\omega) + \mathbf{T}_d(\omega) + \mathbf{T}_\text{fl}(\omega), \quad (47)$$

with the frequency-dependent rotational friction coefficient given by

$$\gamma_r(\omega) = 8\pi\eta R^3(1 - 3\xi) \frac{1 + \alpha R + (\alpha R)^2/3}{1 + \alpha R + \xi(\alpha R)^2}, \quad (48)$$

where $\xi = b/(R + 3b)$.⁴¹ For stick boundary condition ($b = 0$), the known expression⁴² is recovered.

The diffusiophoretic torque is

$$\mathbf{T}_d(\omega) = \frac{3}{2R^2} \gamma_r(\omega) \sum_k b_k \mathbf{r} \times \overline{\nabla c_k(\mathbf{r}, \omega)}^s, \quad (49)$$

while the random torque $\mathbf{T}_\text{fl}(\omega)$ is a Gaussian white noise process with

$$\begin{aligned} \langle \mathbf{T}_\text{fl}(\omega) \rangle &= 0, \\ \langle \mathbf{T}_\text{fl}(\omega) \mathbf{T}_\text{fl}^*(\omega') \rangle &= 4\pi k_B T \text{Re } \gamma_r(\omega) \delta(\omega - \omega') \mathbf{1}. \end{aligned} \quad (50)$$

The frequency dependence of the torque undergoes a similar crossover as for the force around the viscosity characteristic frequency $\omega \sim \nu/R^2$. The low-frequency limit will be taken in Sec. IV.

D. Reaction rate and concentration fields

The advection-diffusion equations (10) and (11) for the concentration fields and their boundary conditions (23) can be linearized if the Péclet numbers are small enough,

$$\text{Pe}_k \equiv \frac{V_d R}{D_k} \ll 1. \quad (51)$$

This condition holds for a micron-size Janus particle moving at the velocity $V_d \sim 10^{-5} \text{ m/s}$ where the solute molecular diffusion coefficients are of order $D_k \sim 10^{-9} \text{ m}^2/\text{s}$ so that $\text{Pe}_k \sim 10^{-2}$. Under such circumstances, the advective term in

Eq. (11) is negligible and we obtain the linearized fluctuating diffusion equation

$$\partial_t c_k = D_k \nabla^2 c_k - \nabla \cdot \boldsymbol{\eta}_k. \quad (52)$$

In terms of the Fourier transforms of the concentration fields,

$$c_k(\mathbf{r}, \omega) = \int_{-\infty}^{+\infty} dt e^{i\omega t} c_k(\mathbf{r}, t), \quad (53)$$

Equation (52) can be written as

$$(-i\omega - D_k \nabla^2) c_k(\mathbf{r}, \omega) + \nabla \cdot \boldsymbol{\eta}_k(\mathbf{r}, \omega) = \sigma_k(\mathbf{r}, \omega), \quad (54)$$

where the source term σ_k is defined on the reactive interface and may be determined using the linearized boundary conditions (23). This source plays a role that is analogous to the induced force density. The diffusion Green functions satisfy the equation

$$(-i\omega - D_k \nabla^2) G_k(\mathbf{r}, \omega) = \delta(\mathbf{r}) \quad (55)$$

and are given by

$$G_k(\mathbf{r}, \omega) = \frac{1}{4\pi D_k r} \exp(-\alpha_k r) \quad \text{with} \quad \alpha_k = \sqrt{-i\omega/D_k} \quad (56)$$

($\text{Re } \alpha_k \geq 0$). The solution of Eq. (54) can be expressed in terms of these Green functions as

$$c_k(\mathbf{r}, \omega) = c_{k0}(\mathbf{r}, \omega) + \int d\mathbf{r}' G_k(\mathbf{r} - \mathbf{r}', \omega) \sigma_k(\mathbf{r}', \omega), \quad (57)$$

where $c_{k0}(\mathbf{r}, \omega)$ is the unperturbed fluctuating concentration field in the absence of the effects of σ_k and is given by the solution of

$$(-i\omega - D_k \nabla^2) c_{k0}(\mathbf{r}, \omega) + \nabla \cdot \boldsymbol{\eta}_k(\mathbf{r}, \omega) = 0. \quad (58)$$

These equations can be solved by methods that are similar to those described above for the velocity field by considering the averages of Eq. (57) over the volume and the surface of the Janus particle.⁵⁰ The following expression for the frequency-dependent reaction rate (28) is found:

$$\begin{aligned} W(\omega) &= 4\pi R D_k \nu_k (1 + \alpha_k R) \left[\overline{c_k(\mathbf{r}, \omega)}^s - \overline{c_{k0}(\mathbf{r}, \omega)}^s \right] \\ &\quad + i\omega \frac{4\pi R^3}{3} \nu_k \overline{c_{k0}(\mathbf{r}, \omega)}^v. \end{aligned} \quad (59)$$

Contrary to Eq. (42) for the force or Eq. (47) for the torque, the expression (59) does not have a closed form. If the catalytic surface was spherical, the frequency-dependent rate would also be given by

$$W(\omega) = 4\pi R^2 \left[\overline{\kappa_+ c_A(\mathbf{r}, \omega)}^s - \overline{\kappa_- c_B(\mathbf{r}, \omega)}^s \right] \quad (60)$$

so that Eqs. (59) and (60) could be combined to obtain an expression involving the surface and volume averages of the unperturbed concentration fields, together with the terms of diffusiophoretic origin. However, Eq. (60) does not hold in the hemispherical geometry of a Janus particle because the rate constants $\kappa_\pm$ vary along the surface of the particle. Therefore, the inversion of Eq. (59) is not straightforward for a Janus particle. However, we see that α_k plays a role similar to α for the velocity field; thus, the frequency dependence should present

a crossover for $|\alpha_k R| \sim 1$, corresponding to the frequency $\omega \sim D_k/R^2$ characteristic of the diffusion of molecular species k . The low-frequency limit will be analyzed in Sec. IV.

In circumstances where the conditions (51) do not hold, we note that the advection-diffusion equations (10) and (11) can be solved by expanding the fields in powers of the Péclet numbers.

IV. LOW-FREQUENCY LIMIT

In this section, we consider the low-frequency limit for the frequency-dependent force (42), torque (47), and rate (59). In this regime, the two conditions $|\alpha R| \ll 1$ and $|\alpha_k R| \ll 1$ are satisfied, corresponding to the frequency range where both $\omega \ll \nu/R^2$ and $\omega \ll D_k/R^2$ apply.

A. Translation and rotation

In the low-frequency limit $\omega \ll \nu/R^2$, the force (42) is expressed in terms of frequency-independent translational friction coefficient

$$\gamma = 6\pi\eta R \frac{1 + 2b/R}{1 + 3b/R}, \quad (61)$$

which is related to the Janus particle diffusion coefficient by the Einstein formula, $D \equiv k_B T/\gamma = (\beta\gamma)^{-1}$. The diffusiophoretic force has the simpler form

$$\mathbf{F}_d(\omega) = \frac{6\pi\eta R}{1 + 3b/R} \sum_k b_k \overline{\mathbf{1}_\perp \cdot \nabla c_k(\mathbf{r}, \omega)}^s. \quad (62)$$

Using the expression (19) for the diffusiophoretic constants, b_k , the diffusiophoretic force and friction coefficient adopt the forms

$$\mathbf{F}_d(\omega) = 6\pi\eta k_B T \sum_k K_k^{(1)} \overline{\mathbf{1}_\perp \cdot \nabla c_k(\mathbf{r}, \omega)}^s \quad (63)$$

and $\gamma = 6\pi\eta R$ for stick boundary conditions, $b = 0$, and

$$\mathbf{F}_d(\omega) = 2\pi R^2 k_B T \sum_k K_k^{(0)} \overline{\mathbf{1}_\perp \cdot \nabla c_k(\mathbf{r}, \omega)}^s \quad (64)$$

and $\gamma = 4\pi\eta R$ for perfect slip boundary conditions, $b = \infty$. The diffusiophoretic force is well defined in both limits.

Also, in the low-frequency limit, the torque (47) is given in terms of the frequency-independent rotational friction coefficient

$$\gamma_r = \frac{8\pi\eta R^3}{1 + 3b/R}, \quad (65)$$

and the diffusiophoretic torque is

$$\mathbf{T}_d(\omega) = \frac{12\pi\eta R}{1 + 3b/R} \sum_k b_k \overline{\mathbf{r} \times \nabla c_k(\mathbf{r}, \omega)}^s. \quad (66)$$

In the limit of perfect stick, we have

$$\mathbf{T}_d(\omega) = 12\pi R k_B T \sum_k K_k^{(1)} \overline{\mathbf{r} \times \nabla c_k(\mathbf{r}, \omega)}^s \quad (67)$$

and $\gamma_r = 8\pi\eta R^3$, which is consistent with a result obtained previously in this limit.³⁶ For perfect slip, we have

$$\mathbf{T}_d(\omega) = 4\pi R^2 k_B T \sum_k K_k^{(0)} \overline{\mathbf{r} \times \nabla c_k(\mathbf{r}, \omega)}^s \quad (68)$$

and $\gamma_r = 0$. For a spherical Janus particle, the diffusiophoretic torque vanishes by cylindrical symmetry, $\mathbf{T}_d(\omega) = 0$, so that only the frictional torque due to viscosity remains.

We note that, in the low-frequency domain $\omega \ll \nu/R^2$, long-time tail effects play a negligible role. For a micrometric particle with $R = 10^{-6}$ m in water, this range extends up to $\omega \ll 10^6$ s⁻¹, corresponding to the microsecond time scale.

B. Diffusion and reaction

For diffusion, the low-frequency regime where $|\alpha_k R| \ll 1$ for all the species k corresponds to the range $\omega \ll D_k/R^2 \sim 10^3$ s⁻¹ for molecular diffusivities of the order of $D_k \sim 10^{-9}$ m²/s. In this regime, the concentration fields take their static profile around the Janus particle and can thus be determined by standard methods.^{51,52}

For a spherical Janus particle of radius R , the stationary concentrations $c_k(r, \theta)$ ($k = A, B$) may be obtained for small enough Péclet numbers (51) by solving the diffusion equations, $\nabla^2 c_k = 0$, subject to the boundary conditions,

$$\begin{aligned} D_k \partial_r c_k|_{r=R} &= -\nu_k \chi(\theta) (\kappa_+ c_A - \kappa_- c_B)_{r=R}, \\ c_k|_{r=\infty} &= \bar{c}_k, \end{aligned} \quad (69)$$

with $\chi(\theta) = H(\cos \theta)$ where the Heaviside function $H(\xi)$ takes the values $H(\xi) = 1$ on the catalytic hemisphere and $H(\xi) = 0$ on the chemically inactive hemisphere. Here, we discard the noise and sink terms in the boundary conditions (23) in order to obtain an analytical expression for the main contribution to the reaction rate. The effects of these terms on the reaction rate will be restored in Sec. V by using the Onsager-Casimir symmetry, but at the level of the overdamped Langevin equations.

The concentration fields of species k around a spherical Janus particle of radius R are given by

$$c_k(r, \theta) = \bar{c}_k + \nu_k \frac{R}{D_k} (\kappa_+ \bar{c}_A - \kappa_- \bar{c}_B) f(r, \theta), \quad (70)$$

where the function $f(r, \theta)$ satisfies the diffusion equation $\nabla^2 f = 0$ with the boundary conditions $R \partial_r f|_R = H(\cos \theta) (Da f - 1)_R$ and $f|_\infty = 0$ in spherical coordinates (r, θ, ϕ) aligned parallel to the particle axis. The boundary condition at the particle surface $r = R$ involves the dimensionless Damköhler number

$$Da \equiv R \left(\frac{\kappa_+}{D_A} + \frac{\kappa_-}{D_B} \right). \quad (71)$$

Letting $k_\pm = 4\pi R^2 \kappa_\pm$, we see that this number takes the form $Da = k_+/k_{D_A} + k_-/k_{D_B}$, where $k_{D_k} = 4\pi D_k R$ are the Smoluchowski diffusion-controlled rate coefficients. In the reaction-limited regime, $k_\pm \ll k_{D_k}$ and $Da \ll 1$, while in the diffusion-controlled regime $k_\pm \gg k_{D_k}$ and $Da \gg 1$.

To obtain the solution, $f(r, \theta)$ is expanded in Legendre functions $P_l(\xi)$, with $\xi = \cos \theta$,

$$f(r, \theta) = \sum_{l=0}^{\infty} a_l P_l(\xi) (R/r)^{l+1}. \quad (72)$$

The coefficients are given by $a_l = \sum_{l'=0}^{\infty} (\mathbf{M}^{-1})_{ll'} \mathcal{A}_{l'}$, where $M_{ll'} = 2(2l+1)^{-1}(l+1)\delta_{ll'} + \text{Da} \mathcal{B}_{ll'}$ with $\mathcal{A}_l = \int_0^1 d\xi P_l(\xi)$ and $\mathcal{B}_{ll'} = \int_0^1 d\xi P_l(\xi) P_{l'}(\xi)$.

Using these results, the mean value of the reaction rate (28) may be written as

$$W_{\text{rxn}} = \Gamma (\kappa_+ \bar{c}_A - \kappa_- \bar{c}_B), \quad (73)$$

with $\Gamma = 2\pi R^2(1 - \text{Da} \gamma_J)$, where

$$\gamma_J = \frac{1}{2\pi R^2} \int_{r=R} dS f(r, \theta) H(\cos \theta) = \sum_{l=0}^{\infty} a_l \mathcal{A}_l. \quad (74)$$

Equivalently, the mean reaction rate is given by Eq. (59) in the limit $\omega = 0$, showing that $\Gamma = 4\pi R^2 a_0$. The surface average of the aforementioned boundary condition satisfied by $f(r, \theta)$ at $r = R$ confirms that $a_0 = (1 - \text{Da} \gamma_J)/2$. The dimensionless coefficients a_0 and γ_J may be obtained by numerical evaluations as a function of the Damköhler number (71). The Appendix gives additional details pertaining to the dependence of γ_J on Da.

At thermodynamic equilibrium, the concentrations $\bar{c}_k$ should satisfy the Guldberg-Waage condition,

$$\frac{\bar{c}_{A,\text{eq}}}{\bar{c}_{B,\text{eq}}} = \frac{\kappa_-}{\kappa_+} = \exp \frac{\Delta\mu^0}{k_B T}, \quad (75)$$

where $\Delta\mu^0 = \mu_B^0 - \mu_A^0$ is the standard free energy of the reaction $A \rightarrow B$. The free energy of the reaction is related to the concentrations by $\Delta\mu = \Delta\mu^0 + k_B T \ln(\bar{c}_B/\bar{c}_A)$, which vanishes at equilibrium, $\Delta\mu_{\text{eq}} = 0$, because of Eq. (75).

Now, the reaction is driven out of equilibrium if the concentrations are not in their equilibrium ratio (75). In this respect, the nonequilibrium control parameter of the reaction is defined in general as the dimensionless chemical affinity

$$A_{\text{rxn}} \equiv \ln \frac{\kappa_+ \bar{c}_A}{\kappa_- \bar{c}_B} = -\frac{\Delta\mu}{k_B T}, \quad (76)$$

which is positive (respectively, negative) for the reaction running in the direction $A \rightarrow B$ (respectively, $B \rightarrow A$) and vanishes at equilibrium.

In the following, we consider the reaction in the linear regime close to equilibrium where the deviations of the concentrations from their equilibrium values, $\delta\bar{c}_k \equiv \bar{c}_k - \bar{c}_{k,\text{eq}}$, are small: $|\delta\bar{c}_k| \ll \bar{c}_{k,\text{eq}}$. In this regime, the chemical affinity can be approximated as

$$A_{\text{rxn}} \simeq \frac{\delta\bar{c}_A}{\bar{c}_{A,\text{eq}}} - \frac{\delta\bar{c}_B}{\bar{c}_{B,\text{eq}}}, \quad (77)$$

up to terms of second order in the concentration deviations $\delta\bar{c}_k$.

Introducing the reaction diffusivity

$$D_{\text{rxn}} \equiv \frac{\Gamma}{2} (\kappa_+ \bar{c}_A + \kappa_- \bar{c}_B), \quad (78)$$

associated with the reaction rate (73), the chemical affinity (77) may also be written close to equilibrium as

$$A_{\text{rxn}} = \frac{W_{\text{rxn}}}{D_{\text{rxn}}}, \quad (79)$$

up to terms with higher powers in the reaction rate (73).

C. The diffusiophoretic force

Since the concentration fields in Eq. (70) are now known, we may write a more explicit expression for the diffusiophoretic force (62),

$$\mathbf{F}_d = \frac{4\pi\eta R}{1 + 3b/R} \left(\frac{b_B}{D_B} - \frac{b_A}{D_A} \right) (\kappa_+ \bar{c}_A - \kappa_- \bar{c}_B) a_1 \mathbf{u}, \quad (80)$$

where we used the fact that

$$\overline{\mathbf{1}_\perp \cdot \nabla f(r, \theta)}^s = \frac{\mathbf{u}}{R} \int_{-1}^{+1} d\xi \xi f(R, \theta) = \frac{2}{3} \frac{a_1}{R} \mathbf{u}. \quad (81)$$

The main features of the dependence of the coefficient a_1 on Da are given in the Appendix. From Eq. (80), we see that the diffusiophoretic force is aligned parallel to the particle axis

$$\mathbf{F}_d = F_d \mathbf{u} \equiv \gamma \chi W_{\text{rxn}} \mathbf{u}, \quad (82)$$

where we have rewritten F_d in the second equality to define the diffusiophoretic parameter χ ,

$$\chi \equiv \frac{F_d}{\gamma W_{\text{rxn}}} = \frac{a_1}{a_0 6\pi R^2 (1 + 2b/R)} \left(\frac{b_B}{D_B} - \frac{b_A}{D_A} \right), \quad (83)$$

which will be useful in what follows. Using the approximation given by Eq. (19) for the diffusiophoretic constants, we have that

$$\chi \simeq \frac{a_1 k_B T}{a_0 6\pi\eta R^2 (1 + 2b/R)} \left(\frac{K_B^{(1)} + bK_B^{(0)}}{D_B} - \frac{K_A^{(1)} + bK_A^{(0)}}{D_A} \right). \quad (84)$$

We see that F_d remains finite in the limits of perfect stick ($b = 0$) and perfect slip ($b \rightarrow \infty$) boundary conditions.

Our calculation does not include corrections due to non-vanishing Péclet numbers.^{36,37}

V. COUPLED LANGEVIN EQUATIONS IN THE OVERDAMPED REGIME

In an earlier study, overdamped Langevin equations for translation, rotation, and reaction were written and used to derive a nonequilibrium mechanochemical fluctuation theorem for diffusiophoretic Janus motors.²³ In this section, we show how these Langevin equations can be derived from the fluctuating thermodynamics formalism presented above, and deduce further results about the nonequilibrium dynamics of Janus motors.

A. Translation

The overdamped regime, where the friction due to viscosity dominates the inertial effects, lies in the domain where $\omega \ll 6\pi\eta R/m = 4.5(\rho/\rho_{\text{sol}})(v/R^2)$. This corresponds to the condition $\omega \ll 10^6 \text{ s}^{-1}$ for a solid particle with mass density $\rho_{\text{sol}} \simeq 4.5 \rho$. In this case, the overdamped regime essentially coincides with the low-frequency domain where the Lorentz condition is satisfied and the long-time tail effects can be neglected.

Using the low-frequency limit of the force, we may immediately write the Langevin equation for a spherical Janus particle of mass m as

$$m \frac{d\mathbf{V}}{dt} = -\gamma \mathbf{V} + \mathbf{F}_d + \mathbf{F}_{\text{ext}} + \mathbf{F}_{\text{fl}}(t), \quad (85)$$

where the translational friction coefficient γ is given in Eq. (61) and the diffusiophoretic force in Eq. (82). We have also added an external force, $\mathbf{F}_{\text{ext}}$. We notice that, in general, the Langevin equation will contain an additional term that accounts for coupling between translation and rotation, $-\gamma_{\text{tr}} \cdot \boldsymbol{\Omega}$, where γ_{tr} is the translation-rotation friction tensor. Since we consider a spherical Janus particle, we have $\gamma_{\text{tr}} = 0$.

According to the Langevin equation, the particle velocity becomes Maxwellian over the thermalization time scale $\tau_t = m/\gamma$. Since the mass is given by $m = (4\pi/3)R^3 \rho_{\text{sol}}$ in terms of the particle mass density ρ_{sol} , the thermalization time becomes $\tau_t = 2\rho_{\text{sol}}R^2/(9\eta)$ if $b \ll R$. For a silica micrometric particle in water at 20 °C, the parameters take the values $\rho_{\text{sol}} \approx 1522 \text{ kg/m}^3$, $\eta \approx 10^{-3} \text{ N s/m}^2$, and $R = 10^{-6} \text{ m}$ so that the thermalization time is estimated to be $\tau_t \approx 3 \times 10^{-7} \text{ s}$. This time scale is short enough to justify considering the overdamped limit where the velocity distribution remains Maxwellian.

In the overdamped limit, the inertial term proportional to the mass m is negligible so, letting $\mathbf{V} = d\mathbf{r}/dt$, the Langevin equation for a spherical Janus particle reduces to

$$\frac{d\mathbf{r}}{dt} = \mathbf{V}_d + \beta D \mathbf{F}_{\text{ext}} + \mathbf{V}_{\text{fl}}(t), \quad (86)$$

where we used $\gamma^{-1} = \beta D$ to write the coefficient of $\mathbf{F}_{\text{ext}}$. The fluctuating velocity field is $\mathbf{V}_{\text{fl}}(t) = \mathbf{F}_{\text{fl}}(t)/\gamma$ and satisfies

$$\begin{aligned} \langle \mathbf{V}_{\text{fl}}(t) \rangle &= 0, \\ \langle \mathbf{V}_{\text{fl}}(t) \mathbf{V}_{\text{fl}}(t') \rangle &= 2D \delta(t - t') \mathbf{1}. \end{aligned} \quad (87)$$

The diffusiophoretic velocity, $\mathbf{V}_d = \mathbf{F}_d/\gamma$, is

$$\mathbf{V}_d = \frac{1}{1 + 2b/R} \sum_k b_k \overline{\mathbf{1}_{\perp} \cdot \nabla c_k(\mathbf{r})}^s = V_d \mathbf{u}, \quad (88)$$

where we have used Eq. (62). The unit vector $\mathbf{u} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$ is taken to lie along the axis of the Janus particle and oriented from the inert toward the catalytic hemisphere. The overdamped Langevin equation (86) has a standard form used in other studies of active Janus particle dynamics; however, the general expression for the diffusiophoretic velocity (88) that includes partial slip differs because of the form of the diffusiophoretic force derived above. In the limit of perfect stick, we obtain the usual expression,³⁴

$$\mathbf{V}_d = \frac{k_B T}{\eta} \sum_k K_k^{(1)} \overline{\mathbf{1}_{\perp} \cdot \nabla c_k(\mathbf{r})}^s, \quad (89)$$

while for perfect slip the result is

$$\mathbf{V}_d = \frac{k_B T R}{\eta} \sum_k K_k^{(0)} \overline{\mathbf{1}_{\perp} \cdot \nabla c_k(\mathbf{r})}^s. \quad (90)$$

The expression (88) for the diffusiophoretic velocity differs from that obtained in Ref. 37 where the denominator $1 + 2b/R$

is absent, but appears in our calculation which is based on the generalized Faxen theorem.^{28,29}

B. Rotation

For a spherical particle with inertia moment $I = 2mR^2/5 = 8\pi\rho_{\text{sol}}R^5/15$, the overdamped regime, where the rotational friction due to viscosity dominates the inertial effects, corresponds to the domain where $\omega \ll 8\pi\eta R^3/I = 15(\rho/\rho_{\text{sol}})(\nu/R^2) \sim 3 \times 10^6 \text{ s}^{-1}$ for a solid particle with mass density $\rho_{\text{sol}} \approx 4.5 \rho$. In this case, the overdamped regime also essentially coincides with the low-frequency domain $\omega \ll \nu/R^2$.

Using Eq. (47), in this regime, the Langevin equation for rotational motion of a Janus particle is given by

$$\mathbf{I} \cdot \frac{d\boldsymbol{\Omega}}{dt} = -\gamma_r \boldsymbol{\Omega} + \mathbf{T}_d + \mathbf{T}_{\text{ext}} + \mathbf{T}_{\text{fl}}(t), \quad (91)$$

where $\mathbf{T}_d$ is a torque due to diffusiophoresis, $\mathbf{T}_{\text{ext}}$ is an external torque, and $\mathbf{T}_{\text{fl}}(t)$ is the Langevin fluctuating torque. Similar to the translational Langevin equation, we have omitted a term that couples rotation to translation ($-\gamma_{\text{rt}} \cdot \mathbf{V}$) since this term vanishes for our Janus particle, as does the diffusiophoretic torque, $\mathbf{T}_d = 0$. The rotational velocity determines the time evolution of the unit vector $\mathbf{u}$ according to

$$\frac{d\mathbf{u}}{dt} = \boldsymbol{\Omega} \times \mathbf{u}. \quad (92)$$

If the Janus particle carries a magnetic moment $\boldsymbol{\mu} = \mu \mathbf{u}$ and the system is subjected to a uniform external magnetic field $\mathbf{B}$, the external torque is given by $\mathbf{T}_{\text{ext}} = \boldsymbol{\mu} \times \mathbf{B}$, which has the effect of orienting the magnetic moment (hence the unit vector) in the direction of the magnetic field $\mathbf{B}$.

If $b \ll R$, the thermalization time of the rotational velocity is given by $\tau_r = I/\gamma_r = \rho_{\text{sol}}R^2/(15\eta) = 3\tau_t/10$, which takes the value $\tau_r \approx 10^{-7} \text{ s}$ for a micrometric particle in water. Again, the time scale is short enough to justify taking the overdamped limit,

$$\begin{aligned} \frac{d\mathbf{u}}{dt} &= -\frac{1}{\gamma_r} \mathbf{u} \times [\mathbf{T}_{\text{ext}} + \mathbf{T}_{\text{fl}}(t)] \\ &= \frac{\mu}{\gamma_r} (\mathbf{B} - \mathbf{B} \cdot \mathbf{u} \mathbf{u}) - \frac{1}{\gamma_r} \mathbf{u} \times \mathbf{T}_{\text{fl}}(t). \end{aligned} \quad (93)$$

Note that this equation does not depend on the particle position or the reactive state so that this stochastic equation is decoupled from the other equations; thus, it drives the direction $\mathbf{u}$ independently of what happens for translation and reaction because the Janus particle is spherical.

C. Reaction

The number n of reactive events during the time interval $[0, t]$ since the beginning of observation is also ruled by a stochastic differential equation

$$\frac{dn}{dt} = W_{\text{rxn}} + W_d + W_{\text{fl}}(t), \quad (94)$$

where W_{rxn} is the aforementioned mean reaction rate, W_d is a contribution from diffusiophoresis to be determined, and $W_{\text{fl}}(t)$ is a fluctuating rate. The rate (94) can be written as $dn/dt = -dN_A/dt = dN_B/dt$ in terms of the numbers of molecules A and B in the solution.

In the overdamped limit, we notice that the contribution W_d is reciprocal to the diffusiophoretic term $\mathbf{V}_d = \mathbf{F}_d/\gamma = \chi W_{\text{rxn}} \mathbf{u}$ in Eq. (86). Since the variables $\mathbf{r}$ and n are even under time reversal, we can use the Onsager symmetry principle in order to determine W_d . First, we identify the affinities or generalized thermodynamic forces as the mechanical and chemical affinities. The chemical affinity A_{rxn} was defined earlier in Eq. (79), while the mechanical affinity is $\mathbf{A}_{\text{mech}} = \beta \mathbf{F}_{\text{ext}}$. Gathering the variables and the affinities in the four-dimensional vectors $\mathbf{X} = (\mathbf{r}, n)$ and $\mathbf{A} = (\mathbf{A}_{\text{mech}}, A_{\text{rxn}})$, the coupled stochastic equations (86) and (94) can be expressed as $dX_\alpha/dt = J_\alpha$ in terms of the currents (4) in the overdamped regime. Since we know that the position $\mathbf{r}$ is ruled by Eq. (86) and that the matrix of linear response coefficients should be symmetric in order to satisfy Onsager's reciprocal relations, we deduce that

$$\mathbf{L} = (L_{\alpha\beta}) = \begin{pmatrix} D\mathbf{1} & \chi D_{\text{rxn}} \mathbf{u} \\ \chi D_{\text{rxn}} \mathbf{u} & D_{\text{rxn}} \end{pmatrix}. \quad (95)$$

This matrix is non-negative to satisfy the second law of thermodynamics. As a consequence of Eqs. (4) and (95), the coupled stochastic differential equations for the position $\mathbf{r}$ and the number n are given by

$$\frac{d\mathbf{r}}{dt} = \chi W_{\text{rxn}} \mathbf{u} + \beta D \mathbf{F}_{\text{ext}} + \mathbf{V}_{\text{fl}}(t), \quad (96)$$

$$\frac{dn}{dt} = W_{\text{rxn}} + \beta \chi D_{\text{rxn}} \mathbf{u} \cdot \mathbf{F}_{\text{ext}} + W_{\text{fl}}(t), \quad (97)$$

with the fluctuating velocity $\mathbf{V}_{\text{fl}}(t)$ and the fluctuating reaction rate $W_{\text{fl}}(t)$ given by the coupled Gaussian white noise processes characterized by Eq. (5) with $[\delta J_\alpha(t)] = [\mathbf{V}_{\text{fl}}(t), W_{\text{fl}}(t)]$. As required, Eq. (96) is identical to Eq. (86) since $V_d = \chi W_{\text{rxn}}$. We emphasize that Eqs. (96) and (97) are coupled to Eq. (93) for rotation. The implication of the reciprocal effect is that an external force combined with an external torque aligning the Janus particle in a preferential orientation can influence the reaction rate.²³

D. The Fokker-Planck equation

The Fokker-Planck equation governing the time evolution of the probability density $p(\mathbf{r}, n, \mathbf{u}; t)$ can be written as

$$\partial_t p = -\partial_{\mathbf{X}} \cdot \mathcal{J} + \hat{L}_{\text{r}} p \quad (98)$$

with the associated current density

$$\mathcal{J} = \mathbf{L} \cdot \mathbf{A} p - \mathbf{L} \cdot \partial_{\mathbf{X}} p \quad (99)$$

expressed in terms of the matrix (95) of linear response coefficients, and the rotational diffusion operator

$$\hat{L}_{\text{r}} p = \frac{D_{\text{r}}}{\sin \theta} \left\{ \partial_\theta [\sin \theta (\partial_\theta p + \beta \mu B \sin \theta p)] + \frac{1}{\sin \theta} \partial_\phi^2 p \right\}, \quad (100)$$

where $D_{\text{r}} \equiv k_B T / \gamma_{\text{r}}$ is the rotational diffusion coefficient. We notice that $\hat{L}_{\text{r}} \mathcal{P}_{\text{r}} = 0$ for the equilibrium rotational distribution

$$\mathcal{P}_{\text{r}}(\mathbf{u}) = \frac{1}{Z_{\text{r}}} \exp(-\beta U) = \frac{1}{Z_{\text{r}}} \exp(\beta \mu B \cos \theta) \quad (101)$$

for the potential energy $U = -\mu \mathbf{B} \cdot \mathbf{u}$ of the magnetic moment in the external magnetic field $\mathbf{B} = (0, 0, B)$ oriented in the z -direction.¹⁷

If rotation is faster than reaction, we may suppose that

$$p(\mathbf{r}, n, \mathbf{u}; t) \simeq \mathcal{P}(\mathbf{r}, n; t) \mathcal{P}_{\text{r}}(\mathbf{u}) \quad (102)$$

with the probability density

$$\mathcal{P}(\mathbf{r}, n; t) = \int d \cos \theta d \phi p(\mathbf{r}, n, \mathbf{u}; t) \quad (103)$$

governed by

$$\begin{aligned} \partial_t \mathcal{P} = & -(\chi W_{\text{rxn}} \langle \mathbf{u} \rangle + \beta D \mathbf{F}_{\text{ext}}) \cdot \nabla \mathcal{P} \\ & - (W_{\text{rxn}} + \beta \chi D_{\text{rxn}} \langle \mathbf{u} \rangle \cdot \mathbf{F}_{\text{ext}}) \partial_n \mathcal{P} \\ & + D \nabla^2 \mathcal{P} + 2 \chi D_{\text{rxn}} \langle \mathbf{u} \rangle \cdot \nabla \partial_n \mathcal{P} + D_{\text{rxn}} \partial_n^2 \mathcal{P}, \end{aligned} \quad (104)$$

where $\langle \cdot \rangle$ denotes a statistical average with respect to the equilibrium canonical distribution (101) for the orientation.

If reaction is faster than rotation, the probability density

$$\mathcal{P}(\mathbf{r}, \mathbf{u}; t) = \int dn p(\mathbf{r}, n, \mathbf{u}; t) \quad (105)$$

is ruled by

$$\partial_t \mathcal{P} + (\chi W_{\text{rxn}} \mathbf{u} + \beta D \mathbf{F}_{\text{ext}}) \cdot \nabla \mathcal{P} = D \nabla^2 \mathcal{P} + \hat{L}_{\text{r}} \mathcal{P}. \quad (106)$$

In the absence of external magnetic field $\mathbf{B} = 0$, there is no preferential orientation so that the rotational motion remains diffusive and controlled by the rotational diffusion time

$$\mathcal{T}_{\text{r}} = \int_0^\infty dt \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle_{\text{eq}} = \frac{1}{2D_{\text{r}}}. \quad (107)$$

In this case, we thus recover the known result¹⁰ that the effective diffusion coefficient is given by $D_{\text{eff}} = D + V_d^2/(6D_{\text{r}})$. The larger the magnitude of the diffusiophoretic velocity V_d , the more enhanced the diffusive random walk of the Janus particle.

A mechanochemical fluctuation theorem,²³ which is a consequence of microreversibility, was derived for the nonequilibrium process ruled by the Fokker-Planck equation (98) with (99).

E. Mechanochemical coupling and efficiencies

In order to investigate the implications of the previous results, we suppose that the external force and the magnetic field are oriented in the z -direction so that $\mathbf{F}_{\text{ext}} = (0, 0, F)$ and $\mathbf{B} = (0, 0, B)$. Therefore, the particle is oriented on average in the same direction: $\langle u_z \rangle = \coth(\beta \mu B) - 1/(\beta \mu B)$. In this case, the averages of Eqs. (96) and (97) give

$$\frac{d\langle z \rangle}{dt} = \chi W_{\text{rxn}} \langle u_z \rangle + \beta D F, \quad (108)$$

$$\frac{d\langle n \rangle}{dt} = W_{\text{rxn}} + \beta \chi D_{\text{rxn}} \langle u_z \rangle F, \quad (109)$$

$d\langle x \rangle/dt = 0$, and $d\langle y \rangle/dt = 0$. Depending on the values of the mechanical and chemical affinities, the mean velocity $\langle z \rangle$ and rate $\langle n \rangle$ can take positive, vanishing, or negative values. Equation (108) shows that the mean velocity vanishes at the stall force $F_{\text{stall}} = -F_d \langle u_z \rangle$, which is proportional to the

diffusiophoretic force $F_d = \gamma \chi W_{\text{rxn}}$. Also, the mean reaction rate is equal to zero at the force $F_0 = -W_{\text{rxn}}/(\beta \chi D_{\text{rxn}} \langle u_z \rangle)$ according to Eq. (109). These two conditions are depicted in Fig. 1 that shows the plane of the mechanical and chemical affinities. For positive values of the chemical affinity A_{rxn} , the propulsion driven by the reaction exerts mechanical work if the force is in the range $F_{\text{stall}} < F < 0$, corresponding to the domain I in Fig. 1. If the force is sufficiently opposed to propulsion to satisfy $F < F_0$, the mean reaction rate (109) can become negative in the domain II, meaning that the reaction is reversed and reactant is synthesized from product, instead of being consumed.

As for molecular motors,⁵³ the efficiency of the mechanical power of the motor can be characterized by

$$\eta_m \equiv -\frac{A_{\text{mech}} \langle \dot{z} \rangle}{A_{\text{rxn}} \langle \dot{n} \rangle}, \quad (110)$$

and the efficiency of the reverse process of synthesis by $\eta_c \equiv 1/\eta_m$. Since the thermodynamic entropy production rate of the coupled processes

$$\frac{1}{k_B} \frac{d_i S}{dt} = A_{\text{mech}} \langle \dot{z} \rangle + A_{\text{rxn}} \langle \dot{n} \rangle \geq 0 \quad (111)$$

is non-negative according to the second law of thermodynamics, the mechanical and chemical efficiencies are bounded by $0 \leq \eta_m \leq 1$ and $0 \leq \eta_c \leq 1$ in their respective domains of application. For a given chemical affinity, the maximal value of the mechanical efficiency is given by

$$\eta^{(\max)} = \frac{1 - \sqrt{1 - q^2}}{1 + \sqrt{1 - q^2}} = \frac{q^2}{4} + \frac{q^4}{8} + O(q^6), \quad (112)$$

where $q \equiv \chi \langle u_z \rangle \sqrt{D_{\text{rxn}}/D}$ satisfies the condition $q^2 \leq 1$. Accordingly, the efficiency of self-propulsion increases with the diffusiophoretic coupling $|\chi|$. A similar expression holds for the chemical efficiency.²³ The locations where the efficiencies reach their maximal values are depicted as dashed lines in Fig. 1. These results show the analogy between self-diffusiophoretic active particles and molecular motors.

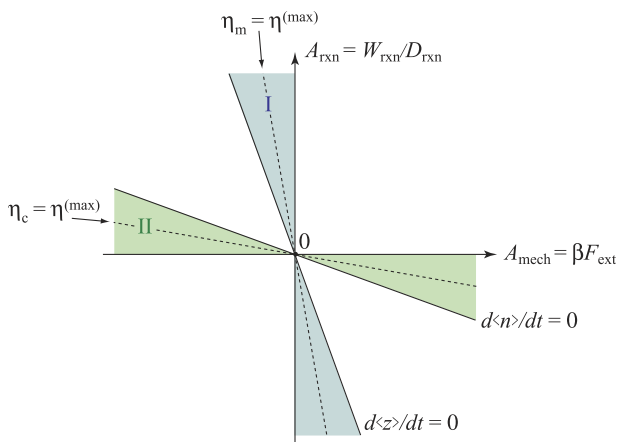


FIG. 1. Schematic representation of the different regimes of the active particle in the plane of the mechanical and chemical affinities. In domain I, diffusiophoretic mechanical work is powered by the reaction. In domain II, an external force of sufficient magnitude acting in a direction opposite to that of the Janus particle velocity can yield the synthesis of fuel from product.

VI. CONCLUSION AND PERSPECTIVES

Equations of motion describing the stochastic dynamics and reaction of an active Janus particle self-propelled by diffusiophoresis were derived in this paper, starting from the fluctuating chemohydrodynamics of the solution surrounding the particle and the boundary conditions for the fluid velocity and concentration fields at the interface with the particle. Utilizing Green-function methods and generalizations of the Faxén theorem,^{28,29,32,38,50} the frequency-dependent force, torque, and reaction rate of the particle were deduced from the boundary conditions and the fluctuating chemohydrodynamic equations. In particular, the diffusiophoretic force and torque exerted on a spherical Janus particle are obtained analytically in terms of the particle radius, the shear viscosity, the slip length, the diffusiophoretic constants, and the concentration gradients at the interface with the solute. Furthermore, an explicit relation is established for the diffusiophoretic coupling parameters. The diffusiophoretic force, torque, and coupling parameter are shown to remain finite in the two limits of perfect stick and slip. In this way, the contributions to the force and torque from friction by the fluid viscosity, diffusiophoresis by the concentration gradients self-generated by the reaction, and the possible presence of an external force and an external torque were determined. From these general equations, coupled overdamped Langevin equations were deduced for the translation, rotation, and reaction of the Janus particle. The stochastic equation for reaction includes a contribution due to mechanochemical coupling that is required in order to satisfy the Onsager-Casimir reciprocal relations to be consistent with microreversibility. This contribution is essential to establish the previously derived mechanochemical fluctuation theorem.²³ The Fokker-Planck equation associated with the coupled stochastic equations was analyzed in several limiting situations. Moreover, the implications of the mechanochemical coupling were studied, in particular, for the efficiencies of energy transduction in the regimes of diffusiophoretic self-propulsion and reciprocal fuel synthesis.

The results obtained in this paper provide fresh perspectives on the understanding of self-propulsion mechanisms of active particles. The calculations can be extended easily to treat other self-phoretic mechanisms including electrophoresis and thermophoresis. For thermophoresis, the coupling of boundary conditions describing thermal slip is known^{21,22} and the methods we have developed can be applied *mutatis mutandis* to this other phoretic mechanism. For electrophoresis, the description should include the electric field generated by the electric charges of the particle and the electrolytic solution.

One can also consider reactions that are more complex than the simple $A \rightleftharpoons B$ reaction that was used to illustrate our results. Indeed, the experimental systems that have been studied typically involve nonlinear reaction networks with possible adsorbates at the surface of the active particle. Accordingly, the surface densities of these adsorbates should be included in the description. The motion of active particles with nonspherical shapes can also be studied. For such active particles, nontrivial coupling between translational and rotational motions is expected in Eqs. (85) and (91).

Furthermore, one can envisage situations where the medium surrounding the active particle is a rarefied or dilute gas, instead of a liquid solution. Such systems may be described by the Boltzmann equation, instead of the Navier-Stokes and diffusion equations. In rarefied gases, the mean free path is larger than the particle radius so that the reactants are essentially in free flight before colliding and reacting at the particle surface. In this case, the transport can be supposed to be ballistic in the gas, as for surface reactions studied in ultra-high vacuum conditions. In dilute gases, the mean free path is smaller than the particle radius so that a local equilibrium will establish itself on the mean free path length scale and intercollisional time scale, whereupon transport is no longer ballistic. The effects of long-time tails on diffusiophoresis could be investigated in such situations.⁴⁶

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APPENDIX: SOLUTION OF REACTION-DIFFUSION EQUATION

Although a set of linear equations must be solved numerically to obtain the concentration fields, insight into the nature of these fields can be obtained by considering the reaction-limited and diffusion-limited regimes.

Since the matrix M in Sec. IV B is the sum of a diagonal matrix and a square matrix multiplied by Da , in the reaction-limited regime it may be approximated by an expansion in powers of Da . The coefficient a_1 takes the value $a_1 = 3/8 = 0.375$ for $Da = 0$. In this limit, we also have $\gamma_J = 0.708\,115$.

In the diffusion-limited regime, there is a thin and strong depletion zone close to the catalytic surface. Accordingly, the problem can be approximately solved by considering a nearly flat catalytic surface. Close to the catalytic surface, the solution is given by

$$f(r, \theta) \simeq \frac{1}{Da + 1} \frac{R}{r}, \quad (A1)$$

while $f \simeq 0$ close to the noncatalytic surface. The solution switches from one form to the other at the contact line between the catalytic and noncatalytic hemispheres, but the contribution of this line is negligible because $Da \gg 1$. Thus, we have

$$f(R, \theta) = \begin{cases} (Da + 1)^{-1}, & \text{on catalytic surface,} \\ 0, & \text{on noncatalytic surface.} \end{cases} \quad (A2)$$

Over the same range of Da values, we have that $a_1 \simeq 0.75 Da^{-1}$ and $\gamma_J \simeq Da^{-1}$ for $Da \rightarrow \infty$. Combining the behavior in both regimes, the coefficient a_1 can be fit by $a_1 \simeq 0.75(Da + 2)^{-1}$. Similarly, we find that γ_J can be approximated by

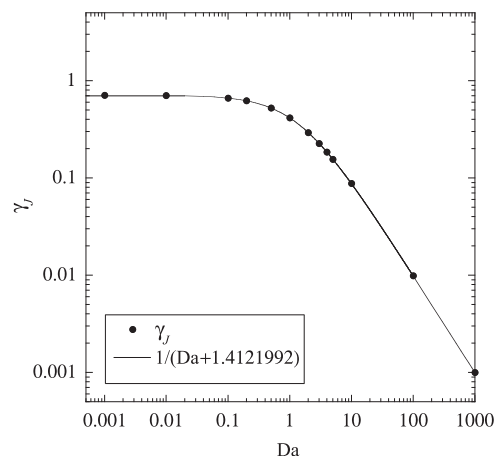


FIG. 2. The coefficient γ_J versus the parameter Da computed with the expansion (72) truncated at $l \leq 30$ (dots) and compared with the fit (line) given by Eq. (A3).

$$\gamma_J \simeq (Da + 1.412\,199\,2)^{-1}, \quad (A3)$$

at the crossover between the reaction- and diffusion-limited regimes, as shown in Fig. 2.

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