Mechanochemical fluctuation theorem and thermodynamics of self-phoretic motors

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Recent advances in synthetic micromotors powered by different self-phoretic mechanisms have been constructed and studied experimentally$^{[1–5]}$. Self-propulsion is achieved by the generation of local gradients of chemical concentrations, electrochemical potential, or temperature, which produce the force driving the motor$^{[6–11]}$. This is the case in particular for Janus motors with catalytic and chemically-inactive hemispheres, moving by diffusiophoresis in a solution with out-of-equilibrium concentrations of fuel and product$^{[11–14]}$. The propulsion mechanism is based on the mechanochemical coupling between the fluid velocity around the motor and the concentration fields induced by the reaction taking place on the catalytic hemisphere. A fundamental issue that arises in this context is the consistency between the thermodynamics of this coupling and the microscopic reversibility of the underlying molecular dynamics. The challenge is that the synthetic motors have micro- or nanometric sizes and, therefore, are subjected to thermal fluctuations due to the atomic structure of matter.

In this letter, we address this issue by deducing coupled Langevin equations for the translational, rotational, and chemical fluctuations of self-phoretic motors, along with a mechanochemical fluctuation theorem. Since the fluctuation theorem is a consequence of microreversibility, we can identify the effect that is reciprocal to the self-diffusiophoretic propulsion. In this way, we show that the chemical reaction can be reversed and the synthesis of fuel from product can be achieved by applying an external force while controlling the directionality of the Janus motor. This reciprocal effect is analogous to what is observed at the nanoscale in molecular motors$^{[15–18]}$.

With this aim in mind, through a systematic analysis, we have determined the boundary conditions coupling the fluid velocity $\mathbf{v} = (v_x, v_y, v_z)$ and the concentration fields $c_k(x,y,z)$ of the different chemical species $k$ on the particle surface within the thin-layer approximation. The molecules of species $k$ in solution are assumed to interact with the surface of the Janus motor by the potential energy $u_k(x,y,z)$ that vanishes beyond the range $\delta$, which is assumed to be small with respect to the particle radius $R$. In this case, the approximation of a locally flat surface holds and the coupled Stokes and diffusion equations can be solved in the thin interaction layer in order to obtain the effective boundary conditions that the fields would satisfy if the layer were arbitrarily thin. Previous work on the thin-layer approximation has been devoted to diffusiophoresis in concentration gradients applied at the macroscale, larger than the particle size$^{[6]}$. For self-diffusiophoresis, the boundary conditions on the concentration fields are modified by the reaction at the surface of the moving particle. Taking the $z$-direction perpendicular and the $(x,y)$-directions parallel to the surface, the slip velocity and the diffusive fluxes are given for such modified conditions by

$$
\left. v_\alpha \right|_{z=0} = \left( b \partial_z v_\alpha - \sum_k b_k \partial_\alpha c_k \right)_{z=0} \quad (\alpha = x, y),
$$

$$
- \left. D_k \partial_z c_k \right|_{z=0} = \nu_k w(x,y) - \sum_{\alpha=x,y} \partial_\alpha \left( \frac{\eta b_k}{k_B T} c_k v_\alpha \right)_{z=0},
$$

up to corrections of higher powers in the thickness $\delta$ of the layer and in the gradient $\partial_\alpha$ parallel to the surface. In Eqs. (1) and (2), $b$ is the slip length$^{[19]}$, $b_k = \frac{k_B T}{\eta} \left( K_k^{(1)} + b K_k^{(0)} \right)$, with $K_k^{(n)} = \int_0^\delta dz z^n \left[ e^{-\beta u_k(z)} - 1 \right]$ is the coefficient of coupling of the surface concentration gradient $\partial_z c_k$ to the slip velocity$^{[6]}$, $\eta$ the fluid shear...
viscosity, $T$ the temperature, $k_B$ Boltzmann’s constant, $D_k$ the diffusion coefficient of solute $k$, $w(x, y)$ the surface reaction rate, and $\nu_k$ the stoichiometric coefficient of species $k$ in the reaction. The last term of Eq. (2) is responsible for the reciprocal effect of the fluid velocity back onto the reaction rate at this level of description.

Employing the boundary conditions [1]–[2] at the surface of the Janus motor, and using Faxen’s theorem in conjunction with a fluctuating hydrodynamics formulation [20, 21], the following Langevin equation is deduced for a spherical particle:

$$\frac{dv}{dt} = -\gamma v + F_d + F_{\text{ext}} + F_{\text{fl}}(t),$$

(5)

where $m$ is the mass of the Janus motor, $v = dr/dt$ its velocity, $\gamma = 6\pi\eta R (1 + \frac{2\ell}{R})/(1 + \frac{6\ell}{R})$ the translational friction coefficient related by Einstein’s relation $\gamma = (\beta D)^{-1}$ to the diffusion coefficient $D$ [21],

$$F_d = \frac{6\pi\eta R}{1 + \frac{6\ell}{R}} \sum_k b_k (1 - nn) \cdot \nabla c_k(r, t),$$

(6)

the diffusiophoretic force involving the surface average $\langle \cdot \rangle = \int_{r=R}^r(r) dS/(4\pi R^2)$ (n being a unit vector perpendicular to the surface), $F_{\text{ext}}$ an external force (e.g. the gravitational force) [3], and $F_{\text{fl}}(t)$ the Langevin fluctuating force. The diffusiophoretic force is directed along the axis of the Janus motor, specified by the unit vector $u$: $F_d = F_d u$. Moreover, this force is proportional to the mean reaction rate $W_{\text{rxn}}$ through the surface gradient of the concentration fields. Accordingly, we introduce the diffusiophoretic coupling coefficient $\chi = F_d/(\gamma W_{\text{rxn}})$. Using the definitions of $F_d$ and $\gamma$ given above, the explicit dependence of $\chi$ on the slip length $b$ can be written in the form $\chi \sim (C^{(1)} + bC^{(0)})/(1 + \frac{2\ell}{R})$ where the quantities $C^{(n)}$ are given in terms of the constants [4] and the molecular diffusivities $D_k$ of species $k = A, B$. From this expression we see that $\chi$ has a well-defined value in both the limit $b = 0$ for stick boundary conditions and the limit $b = \infty$ for perfect slip boundary conditions. An enhancement of the diffusiophoretic effects is expected if the hydrophobicity is large because $\chi \sim (\delta/R)^\ell$ with $\ell = 2$ if $b = 0$, but with $\ell = 1$ if $b \to \infty$.

In the overdamped limit, the Langevin equation (5) becomes

$$\frac{dr}{dt} = V_d u + \beta D F_{\text{ext}} + V_{\text{fl}}(t),$$

(7)

where $r = (x, y, z)$ is the particle position, $V_d = \chi W_{\text{rxn}} = F_d/\gamma$ is the diffusiophoretic velocity and $V_{\text{fl}}(t) = F_{\text{fl}}(t)/\gamma$ the fluctuating velocity.

The orientation $u$ of the Janus particle is ruled by the following rotational overdamped Langevin equation:

$$\frac{du}{dt} = -\frac{1}{\gamma_{\text{rot}}} u \times [T_{\text{ext}} + T_{\text{fl}}(t)],$$

(8)

where $\gamma_{\text{rot}} = 8\pi\eta R^3/(1 + \frac{9\ell}{R})$ is the rotational friction coefficient [22], $T_{\text{ext}} = \mu u \times B$ is an external torque due to an external magnetic field $B$ exerted on a magnetic dipole $\mu$ attached to the particle or the gravitational field acting on the nonuniform mass density of the Janus particle [22], and $T_{\text{fl}}(t)$ is the Langevin fluctuating torque associated with the rotational diffusion coefficient $D_{\text{rot}} = k_B T/\gamma_{\text{rot}}$. Since the Janus motor is assumed to be spherical, there is no torque due to diffusiophoresis. We note that the external force and torque derive from the potential energy $U(r, u) = -F_{\text{ext}} \cdot r - \mu B \cdot u$.

In order to describe the mechemanochemical coupling, Eqs. (11) and (13) must be supplemented by a stochastic equation for the chemical reaction. Here, we consider the simple reaction $A \rightleftharpoons B$, where $A$ is the fuel and $B$ the product, so that the mean reaction rate is given by $W_{\text{rxn}} = \Gamma(\bar{c}_A - \bar{c}_B)$ in terms of the rate constants $k_{\pm}$ and the concentrations $\bar{c}_A$ and $\bar{c}_B$ at an arbitrarily large distance from the Janus particle, up to a dimensionless constant $\Gamma$. The mean reaction rate vanishes at chemical equilibrium when $\bar{c}_A/\bar{c}_B = k_-/k_+$. In order to satisfy microreversibility, the chemical stochastic equation must take the form,

$$\frac{dn}{dt} = W_{\text{rxn}} + \beta \chi D_{\text{rxn}} u \cdot F_{\text{ext}} + W_{\text{fl}}(t),$$

(9)

where the second term on the right $(\beta \chi D_{\text{rxn}} u \cdot F_{\text{ext}})$ is a reciprocal contribution of the external force back onto the reaction rate due to the diffusiophoretic coupling and proportional to the reaction diffusivity $D_{\text{rxn}}$. The velocity and rate fluctuations are coupled Gaussian white noises characterized by

$$\langle V_{\text{fl}}(t) \rangle = 0, \quad \langle W_{\text{fl}}(t) \rangle = 0,$$

(10)

$$\langle V_{\text{fl}}(t) \otimes W_{\text{fl}}(t') \rangle = 2D \delta(t - t') 1,$$

(11)

$$\langle W_{\text{fl}}(t) W_{\text{fl}}(t') \rangle = 2D_{\text{rxn}} \delta(t - t'),$$

(12)

$$\langle V_{\text{fl}}(t) W_{\text{fl}}(t') \rangle = 2\chi D_{\text{rxn}} u \delta(t - t'),$$

(13)

where $\otimes$ denotes the tensorial product and $1$ the $3 \times 3$ identity matrix. The necessity of including the reciprocal contribution can be seen by considering the evolution equations for the mean position $r$ and number $n$. Letting $X = (r, n)$, these equations are

$$\frac{dX}{dt} = L \cdot A,$$  

(14)

where $A = (A_{\text{mech}}, A_{\text{rxn}})$ is the vector of the generalized thermodynamic forces comprising the mechanical affinity, $A_{\text{mech}} = \beta F_{\text{ext}}$, and chemical affinity, $A_{\text{rxn}} = W_{\text{rxn}}/D_{\text{rxn}}$ [24, 25], while the matrix $L$ is given by

$$L = \begin{pmatrix} 0 & \chi D_{\text{rxn}} u \\ \chi D_{\text{rxn}} u & 0 \end{pmatrix},$$

(15)

with $L = L^T$ to be consistent with Onsager’s reciprocal relations. In order to satisfy the second law of
thermodynamics, the diffusivities should satisfy $D \geq 0$, $D_{\text{rxn}} \geq 0$, and $D \geq \chi^2 D_{\text{rxn}}$. The control parameters are the mean reaction rate $W_{\text{rxn}}$ determined by the solute concentrations, the external force $F_{\text{ext}}$, and the external torque $T_{\text{ext}}$. An important aspect is that only the mean reaction rate and the external force can drive the Janus particle into a nonequilibrium steady state. Indeed, the external torque has here the sole effect of aligning the Janus particle parallel to the external magnetic or gravitational field, but does not generate a gyration of the particle as in Ref. \[26\]. Accordingly, the probability distribution of the particle orientation reaches equilibrium after the rotational relaxation time $\tau_{\text{rot}} = 1/(2D_{\text{rot}})$ and no longer contributes to the entropy production rate,

$$\frac{1}{k_B} \frac{dS}{dt} = \beta F_{\text{ext}} \cdot \langle \dot{r} \rangle + A_{\text{rxn}} \langle \dot{n} \rangle \geq 0. \quad (16)$$

The mechanochemical fluctuation theorem corresponding to the entropy production \(16\) is given by

$$\frac{P(r, n; t)}{P(-r, -n; t)} \simeq \exp \left( \beta F_{\text{ext}} \cdot r + A_{\text{rxn}} n \right) \quad (17)$$

for the joint probability density $P(r, n; t)$ to find the motor at the position $r$ after $n$ reactive events have occurred during the time interval $t$. This should be longer than the rotational relaxation time, as well as the characteristic time of solute molecular diffusion (which is of the order of $\tau_{\text{diff}, k} \sim R^2/D_k$ in the diffusion-limited regime). The fluctuation theorem \(17\) can be deduced from the Fokker-Planck equation for the coupled Langevin equations by using methods of large-deviation theory \[18, 27, 28\]. This theorem extends previous relations \[26, 29, 30\] by including the chemical fluctuations, which are essential to obtain all of the contributions to the entropy production and prove its non-negativity \(16\) by Jensen’s inequality (exp $x$) $\geq$ exp($\langle x \rangle$). Figure 1 shows that the mechanochemical fluctuation theorem is satisfied.

Suppose that the particle is subjected to an external force in the $z$-direction $F_{\text{ext}} = (0, 0, F)$, as well as to the external magnetic field $B = (0, 0, B)$ so that the particle is oriented on average in that direction: $\langle u_z \rangle = \coth(\beta \mu B) - 1/(\beta \mu B)$. Often, only the position is observed while the rate is very large. Since the probability distribution becomes Gaussian after a long enough time by the central limit theorem, we recover the effective fluctuation relation \(30\) for the displacement along the $z$-direction

$$\mathcal{P}(z; t) \propto \exp \frac{F_{\text{eff}} z}{k_B T_{\text{eff}}}, \quad (18)$$

which is expressed in terms of an effective force $F_{\text{eff}} = F + F_\lambda \langle u_z \rangle$ resulting from the external and diffusiophoretic forces, and the effective temperature $T_{\text{eff}} = T [1 + (V_\lambda^2/F_\lambda^2) \int_0^\infty C_{zz}(t) dt]$ where $C_{zz}(t) \equiv \langle \{u_z(t) - \langle u_z \rangle \} \{u_z(t) - \langle u_z \rangle \} \rangle$ is the time-dependent correlation function of the orientation along the $z$-direction. In the absence of an external force and torque ($F = 0$ and $B = 0$), we also recover the known result that diffusion is enhanced due to the self-phoretic effect, the effective translational diffusion coefficient being given by $D_{\text{eff}} = D + V_\lambda^2/(6D_{\text{rot}})$.

In the presence of external force and torque, the Janus particle can move against the external force, as shown in Fig. 2. The condition is that the force $F$ takes a value between the stall force $F_{\text{stall}} = -V_\lambda \langle u_z \rangle/(\beta D)$ and zero.

A key point is that the fluctuation theorem \(17\) would not hold without the reciprocal term due to the diffusiophoretic coupling $\chi$ in Eq. \(9\). A most important
The thermodynamic efficiency $\eta$ in Supplementary Material [32].

stall force and $f_{\text{stall}}$ denotes the rescaled stall force and $f_0$ the threshold between fuel synthesis and consumption. The Janus particle is propelled against the external force in the interval I. Fuel synthesis happens in the interval II.

FIG. 2. Janus particle subjected to an external force and magnetic field oriented in the z-direction: The mean values of the fluctuating rescaled velocities $\tilde{v}_z = \tilde{v}_z/\sqrt{\langle DD_{\text{rot}} \rangle}$ versus the rescaled magnitude of the external force $f = \beta F/\sqrt{\langle DD_{\text{rot}} \rangle}$ for the parameter values $p = \mu B = 2$, $w = W_{\text{rxn}}/\sqrt{\langle DD_{\text{rot}} \rangle} = 0.8$, and $c = \chi\sqrt{\langle DD_{\text{rot}} \rangle} = 0.8$. The dots show the results of a numerical simulation with a statistics of $10^5$ trajectories integrated over the time interval $t_0 = 10$, using the method described in Supplementary Material [32]. $f_{\text{stall}}$ denotes the rescaled stall force and $f_0$ the threshold between fuel synthesis and consumption. The Janus particle is propelled against the external force in the interval I. Fuel synthesis happens in the interval II.

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Supplementary Material

The aim of this supplementary material is to describe the numerical method used to simulate the process based on the coupled overdamped Langevin equations given by

\[
\frac{du}{dt} = \omega_{\text{ext}} \times u + \omega_n(t) \times u,
\]

\[
\frac{dv}{dt} = \chi W_{\text{rxn}} u + \beta D F_{\text{ext}} + V_{\text{ext}}(t),
\]

\[
\frac{dw}{dt} = W_{\text{rxn}} + \beta \chi D_{\text{rxn}} u \cdot F_{\text{ext}} + W_{\text{ext}}(t),
\]

with the angular velocity due to the external magnetic field \( \mathbf{B} \) exerted on the magnetic dipole \( \mu \) of the Janus particle

\[
\omega_{\text{ext}} = \frac{1}{T_{\text{rot}}} T_{\text{ext}} = \frac{\mu}{T_{\text{rot}}} u \times \mathbf{B}.
\]

The fluctuating angular velocity \( \omega_n(t) = T_{\text{rot}}(t)/T_{\text{rot}} \), the fluctuating velocity \( V_n(t) = F_{\text{ext}}(t)/\gamma \), and the fluctuating reaction rate \( W_n(t) \) are coupled Gaussian white noises characterized by

\[
\langle \omega_n(t) \rangle = 0, \quad \langle V_n(t) \rangle = 0, \quad \langle W_n(t) \rangle = 0,
\]

\[
\langle \omega_n(t) \otimes \omega_n(t') \rangle = 2D_{\text{rot}} \delta(t - t') 1,
\]

\[
\langle V_n(t) \otimes V_n(t') \rangle = 2D \delta(t - t') 1,
\]

\[
\langle W_n(t) W_n(t') \rangle = 2D_{\text{rxn}} \delta(t - t'),
\]

\[
\langle V_n(t) W_n(t') \rangle = 2\chi D_{\text{rxn}} u \delta(t - t').
\]

We notice that the stochastic equation for rotation is decoupled from the ones for translation and rotation. The fluctuating rotational motion is simulated by the method of quaternions \[34,35\]. The different noises can thus be decoupled as follows:

\[
\omega_n(t) = \sqrt{2D_{\text{rot}}} \xi_{\text{rot}}(t),
\]

\[
V_n(t) = \sqrt{2D} \xi_1(t) u_1 + \sqrt{2D} \xi_2(t) u_2 + \left[ \sqrt{D\lambda_+} \xi_3(t) - \sqrt{D\lambda_-} \xi_4(t) \right] u_3,
\]

\[
W_n(t) = \sqrt{D_{\text{rxn}}} \lambda_+ \xi_3(t) + \sqrt{D_{\text{rxn}}} \lambda_- \xi_4(t),
\]

in terms of the independent Gaussian white noises satisfying

\[
\langle \xi_{\text{rot}}(t) \rangle = 0, \quad \langle \xi_{\text{rot}}(t) \otimes \xi_{\text{rot}}(t') \rangle = \delta(t - t') 1,
\]

\[
\langle \xi_i(t) \xi_j(t') \rangle = \delta(t - t') \delta_{ij},
\]

the parameters

\[
\lambda_\pm = 1 \pm \sqrt{\chi^2 D_{\text{rxn}} / D}, \quad \chi = \chi / |\chi|,
\]

and the unit vectors \( \{u_1, u_2, u_3 = u\} \) attached to the frame of the Janus particle. The unit vector \( u_3 = u \) is oriented along the particle axis pointing from the inactive towards the catalytic hemisphere, while the unit vectors \( u_1 \) and \( u_2 \) are perpendicular to the axis.

Introducing the rescaled dimensionless variables

\[
t_\ast \equiv D_{\text{rot}} t, \quad u_\ast \equiv \sqrt{\frac{D_{\text{rot}} D}{D}} u, \quad n_\ast \equiv \sqrt{\frac{D_{\text{rot}} D_{\text{rxn}}}{D}} n,
\]

See Supplementary Material for the description of the numerical method used to simulate the stochastic process.

\[32\]

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\[31\]

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and the dimensionless parameters
\[ p \equiv \beta \mu B, \quad (37) \]
\[ f \equiv \beta F \sqrt{\frac{D}{D_{\text{rot}}}}, \quad (38) \]
\[ w \equiv \frac{W_{\text{ext}}}{\sqrt{D_{\text{ext}}D_{\text{rot}}}}, \quad (39) \]
\[ c \equiv \chi \sqrt{\frac{D_{\text{ext}}}{D}}, \quad (40) \]
the stochastic differential equations read
\[
\frac{du}{dt^*} = p (u \times 1_p) \times u + \sqrt{2} \hat{\xi}_{\text{rot}}(t^*) \times u, \quad (41) \\
\frac{dr}{dt^*} = f 1_f + cwu + \sqrt{2} \hat{\xi}_1(t^*) u_1 + \sqrt{2} \hat{\xi}_2(t^*) u_2 + \left[ \sqrt{\lambda_+} \hat{\xi}_3(t^*) - \sqrt{\lambda_-} \hat{\xi}_4(t^*) \right] u, \quad (42) \\
\frac{dn}{dt^*} = w + cfu \cdot 1_f + \sqrt{\lambda_+} \hat{\xi}_3(t^*) + \sqrt{\lambda_-} \hat{\xi}_4(t^*) , \quad (43)
\]
with the unit vectors \( u = u_3, \ 1_p = B/|B|, \ 1_f = F_{\text{ext}}/|F_{\text{ext}}|, \) and the dimensionless independent Gaussian white noises \( \hat{\xi}_{\text{rot}}(t^*) \) and \( \hat{\xi}_i(t^*) \) satisfying Eqs. (31)-(32) but with the time \( t \) replaced by the dimensionless time \( t^* \) defined by Eq. (34).

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