

Communication: Mechanochemical fluctuation theorem and thermodynamics of self-phoretic motors

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Microscopic dynamical aspects of the propulsion of nanomotors by self-phoretic mechanisms are considered. Propulsion by self-diffusiophoresis relies on the mechanochemical coupling between the fluid velocity field and the concentration fields induced by asymmetric catalytic reactions on the motor surface. The consistency between the thermodynamics of this coupling and the microscopic reversibility of the underlying molecular dynamics is investigated. For this purpose, a mechanochemical fluctuation theorem for the joint probability to find the motor at position $\mathbf{r}$ after n reactive events have occurred during the time interval t is derived, starting from coupled Langevin equations for the translational, rotational, and chemical fluctuations of self-phoretic motors. An important result that follows from this analysis is the identification of an effect that is reciprocal to self-propulsion by diffusiophoresis, which leads to a dependence of the reaction rate on the value of an externally applied force. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5008562>

Recently, 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.^{6–10} 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.^{10–13} 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. Mechanochemical coupling has been considered in a number of different contexts for molecular machines and swimmers undergoing conformational changes.^{14–17} Work has also been devoted to the thermodynamics of collections of such motors without considering the role of this coupling.^{18–20} A fundamental issue that arises in this context is the consistency between the thermodynamics of this coupling and the microreversibility of the underlying molecular dynamics. The challenge is that the synthetic motors have micrometric or nanometric sizes and, therefore, are subjected to thermal fluctuations due to the atomic structure of matter.

In this communication, we address this issue by deducing a mechanochemical fluctuation theorem starting from coupled Langevin equations for the translational, rotational, and chemical fluctuations of self-phoretic motors. Since the fluctuation theorem is a consequence of microreversibility,^{21–26} we can identify the effect that is reciprocal to the self-diffusiophoretic

propulsion. In this way, we show that the reaction rate is influenced by an external force and an external torque, and can be reversed in the linear regime close to thermodynamic equilibrium, possibly leading to the synthesis of fuel from product. This reciprocal effect is analogous to what is observed at the nanoscale for molecular motors.^{14,23,27,28}

With this aim in mind, we consider the following Langevin equation for a spherical particle:²⁹

$$m \frac{d\mathbf{V}}{dt} = -\gamma \mathbf{V} + \mathbf{F}_d + \mathbf{F}_{\text{ext}} + \mathbf{F}_\Pi(t), \quad (1)$$

where m is the mass of the Janus motor, $\mathbf{V} = d\mathbf{r}/dt$ is its velocity, $\gamma = k_B T/D$ is the translational friction coefficient related by Einstein's relation to the particle diffusion coefficient D , $\mathbf{F}_d = F_d \mathbf{u}$ is the diffusiophoretic force directed along the axis of the Janus motor specified by the unit vector $\mathbf{u}$, $\mathbf{F}_{\text{ext}}$ is an external force, and $\mathbf{F}_\Pi(t)$ is the Langevin fluctuating force. Since the diffusiophoretic force F_d is proportional to the mean reaction rate W_{rxn} , we introduce the diffusiophoretic coupling coefficient

$$\chi \equiv \frac{F_d}{\gamma W_{\text{rxn}}}. \quad (2)$$

In the overdamped limit, the Langevin equation (1) becomes

$$\frac{d\mathbf{r}}{dt} = V_d \mathbf{u} + \beta D \mathbf{F}_{\text{ext}} + \mathbf{V}_\Pi(t), \quad (3)$$

where $\mathbf{r} = (x, y, z)$ is the particle position, $V_d = \chi W_{\text{rxn}} = F_d/\gamma$ is the diffusiophoretic velocity, $\beta = (k_B T)^{-1}$ is the inverse temperature, and $\mathbf{V}_\Pi(t) = \mathbf{F}_\Pi(t)/\gamma$ is the fluctuating velocity.

The orientation $\mathbf{u}$ of the Janus particle is ruled by the following rotational overdamped Langevin equation:^{30,31}

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$$\frac{d\mathbf{u}}{dt} = -\frac{1}{\gamma_{\text{rot}}} \mathbf{u} \times [\mathbf{T}_{\text{ext}} + \mathbf{T}_{\text{fl}}(t)], \quad (4)$$

where γ_{rot} is the rotational friction coefficient,³² $\mathbf{T}_{\text{ext}}$ is an external torque due to an external magnetic field $\mathbf{B}$ exerted on a magnetic dipole $\mu\mathbf{u}$ attached to the particle,³³ $\mathbf{T}_{\text{ext}} = \mu\mathbf{u} \times \mathbf{B}$, or due to a gravitational field acting on the nonuniform mass density of the Janus particle,³⁴ and $\mathbf{T}_{\text{fl}}(t)$ is the Langevin fluctuating torque associated with the rotational diffusion coefficient $D_{\text{rot}} = (\beta\gamma_{\text{rot}})^{-1}$. Since the Janus motor is assumed to be spherical, there is no torque due to diffusiophoresis. We note that the external force and torque are derived from the potential energy $U(\mathbf{r}, \mathbf{u}) = -\mathbf{F}_{\text{ext}} \cdot \mathbf{r} - \mu\mathbf{B} \cdot \mathbf{u}$.

In order to describe the mechanochemical coupling, Eqs. (3) and (4) must be supplemented by a stochastic equation for the reaction. Here, we consider the simple reaction $A \rightleftharpoons B$, where A is the fuel and B is the product, so that the mean reaction rate is given by $W_{\text{rxn}} = k_+ \bar{c}_A - k_- \bar{c}_B$ in terms of the rate constants $k_{\pm}$ and the concentrations $\bar{c}_A$ and $\bar{c}_B$ far from the Janus particle. The mean reaction rate vanishes at chemical equilibrium when $\bar{c}_A/\bar{c}_B = k_-/k_+$. Forward reactive events $A \rightarrow B$ predominate over their equilibrium number if $\bar{c}_A > k_- \bar{c}_B/k_+$, corresponding to net production of product, $W_{\text{rxn}} > 0$, while $W_{\text{rxn}} < 0$ if $\bar{c}_B > k_+ \bar{c}_A/k_-$ and reverse events $B \rightarrow A$ predominate corresponding to net production of fuel. These considerations allow one to identify the state of thermodynamic equilibrium and choose concentrations $\bar{c}_A$ and $\bar{c}_B$ so that system is in the linear regime close to it.

To satisfy microreversibility, a reciprocal contribution of the external force back onto the reaction rate must be taken into account. The necessity of including this contribution can be seen by considering the evolution equations for the mean position $\mathbf{r}$ and net number n of reactive events yielding product in the linear regime close to equilibrium. Letting $\mathbf{X} = (\mathbf{r}, n)$, these equations are

$$\frac{d\langle \mathbf{X} \rangle}{dt} = \mathbf{L} \cdot \mathbf{A}, \quad (5)$$

where $\mathbf{A} = (\mathbf{A}_{\text{mech}}, A_{\text{rxn}})$ is the vector of the generalized thermodynamic forces comprising the mechanical affinity, $\mathbf{A}_{\text{mech}} = \beta \mathbf{F}_{\text{ext}}$, and the chemical affinity in the linear regime, $A_{\text{rxn}} = W_{\text{rxn}}/D_{\text{rxn}}$.^{22,26} The matrix $\mathbf{L}$ is given by

$$\mathbf{L} = \begin{pmatrix} D \mathbf{1} & \chi D_{\text{rxn}} \mathbf{u} \\ \chi D_{\text{rxn}} \mathbf{u} & D_{\text{rxn}} \end{pmatrix}, \quad (6)$$

with $\mathbf{L} = \mathbf{L}^T$ to be consistent with Onsager's reciprocal relations when the Janus particle has the instantaneous orientation $\mathbf{u}$, which is ruled by Eq. (4). Consequently, the chemical stochastic equation must take the form

$$\frac{dn}{dt} = W_{\text{rxn}} + \beta \chi D_{\text{rxn}} \mathbf{u} \cdot \mathbf{F}_{\text{ext}} + W_{\text{fl}}(t), \quad (7)$$

where the second term on the right ($\beta \chi D_{\text{rxn}} \mathbf{u} \cdot \mathbf{F}_{\text{ext}}$) is the reciprocal contribution due to the diffusiophoretic coupling. The velocity and rate fluctuations are coupled Gaussian white noises characterized by

$$\langle \mathbf{V}_{\text{fl}}(t) \rangle = 0, \quad \langle W_{\text{fl}}(t) \rangle = 0, \quad (8)$$

$$\langle \mathbf{V}_{\text{fl}}(t) \otimes \mathbf{V}_{\text{fl}}(t') \rangle = 2D \delta(t - t') \mathbf{1}, \quad (9)$$

$$\langle W_{\text{fl}}(t) W_{\text{fl}}(t') \rangle = 2D_{\text{rxn}} \delta(t - t'), \quad (10)$$

$$\langle \mathbf{V}_{\text{fl}}(t) W_{\text{fl}}(t') \rangle = 2\chi D_{\text{rxn}} \mathbf{u} \delta(t - t'), \quad (11)$$

where $\otimes$ denotes the tensorial product and $\mathbf{1}$ denotes the 3×3 identity matrix. 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_{rxn} determined by the solute concentrations, the external force $\mathbf{F}_{\text{ext}}$, and the external torque $\mathbf{T}_{\text{ext}}$. 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^{33,34} but does not generate a gyration of the particle as in Ref. 35. 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,^{36–38}

$$\frac{1}{k_B} \frac{d_i S}{dt} = \beta \mathbf{F}_{\text{ext}} \cdot \langle \dot{\mathbf{r}} \rangle + A_{\text{rxn}} \langle \dot{n} \rangle \geq 0. \quad (12)$$

The mechanochemical fluctuation theorem corresponding to the entropy production (12) is given by

$$\frac{P(\mathbf{r}, n; t)}{P(-\mathbf{r}, -n; t)} \simeq \exp(\beta \mathbf{F}_{\text{ext}} \cdot \mathbf{r} + A_{\text{rxn}} n) \quad (13)$$

for the joint probability density $P(\mathbf{r}, n; t)$ to find the motor at the position $\mathbf{r}$ after n reactive events have occurred during the time interval t . This latter should be longer than the rotational relaxation time, as well as the characteristic time of solute molecular diffusion.

The fluctuation theorem (13) can be deduced from the Fokker-Planck equation for the time evolution of the probability density $p(\mathbf{X}, \mathbf{u}; t)$ associated with the coupled Langevin equations,

$$\partial_t p = -\partial_{\mathbf{X}} \cdot (\mathbf{L} \cdot \mathbf{A} p - \mathbf{L} \cdot \partial_{\mathbf{X}} p) + \hat{L}_{\text{rot}} p \equiv \hat{L} p, \quad (14)$$

with the matrix $\mathbf{L}$ given by Eq. (6) and

$$\hat{L}_{\text{rot}} p = \frac{D_{\text{rot}}}{\sin \theta} \left\{ \partial_{\theta} [\sin \theta (\partial_{\theta} p + \beta \mu B \sin \theta p)] + \frac{1}{\sin \theta} \partial_{\phi}^2 p \right\}, \quad (15)$$

if $\mathbf{B} = (0, 0, B)$ and $\mathbf{u} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$. The fluctuation theorem can be proved by introducing the cumulant generating function^{21,23,26}

$$\mathcal{Q}(\boldsymbol{\lambda}) \equiv \lim_{t \rightarrow \infty} -\frac{1}{t} \ln \langle e^{-\boldsymbol{\lambda} \cdot \mathbf{X}} \rangle_t \quad (16)$$

with the auxiliary parameters $\boldsymbol{\lambda} = (\boldsymbol{\lambda}_r, \lambda_n)$ used to generate the cumulants by successive derivations. The angular bracket $\langle \cdot \rangle_t$ denotes an average over the probability density $p(\mathbf{X}, \mathbf{u}; t)$. This latter evolves in time according to $p = e^{\hat{L}t} p_0$ from the initial distribution p_0 . Accordingly, the average in Eq. (16) can be transformed as

$$\langle e^{-\boldsymbol{\lambda} \cdot \mathbf{X}} \rangle_t = \int d\mathbf{X} d\mathbf{u} e^{-\boldsymbol{\lambda} \cdot \mathbf{X}} e^{\hat{L}t} p_0 = \int d\mathbf{X} d\mathbf{u} e^{\hat{L}\lambda t} e^{-\boldsymbol{\lambda} \cdot \mathbf{X}} p_0 \quad (17)$$

by introducing the modified operator

$$\begin{aligned}\hat{L}_\lambda &\equiv e^{-\lambda \cdot \mathbf{X}} \hat{L} e^{\lambda \cdot \mathbf{X}} \\ &= -\mathbf{A} \cdot \mathbf{L} \cdot (\partial_{\mathbf{X}} + \boldsymbol{\lambda}) + (\partial_{\mathbf{X}} + \boldsymbol{\lambda}) \cdot \mathbf{L} \cdot (\partial_{\mathbf{X}} + \boldsymbol{\lambda}) + \hat{L}_{\text{rot}}.\end{aligned}\quad (18)$$

In the long-time limit, the expression (17) will decay at a rate given by the leading eigenvalue of the modified operator that is the solution of the following eigenvalue equation:²¹

$$\hat{L}_\lambda \Psi = -Q(\lambda) \Psi. \quad (19)$$

The modified operator (18) has the symmetry

$$\eta^{-1} \hat{L}_\lambda \eta = \hat{L}_{\mathbf{A}-\boldsymbol{\lambda}}^\dagger \quad (20)$$

expressed in terms of the Boltzmann factor

$$\eta = \exp(\beta \mu B \cos \theta), \quad (21)$$

where the adjoint of the operator is defined with respect to the scalar product $\langle g|f \rangle \equiv \int d\mathbf{X} d\mathbf{u} g^* f$. The symmetry (20) is established by noting that $\eta^{-1} \hat{L}_{\text{rot}} \eta = \hat{L}_{\text{rot}}^\dagger$ and by using $\partial_{\mathbf{X}}^\dagger = -\partial_{\mathbf{X}}$ in the first two terms of Eq. (18).^{21,23,26} As a consequence, the cumulant generating function obeys the symmetry relation

$$Q(\lambda) = Q(\mathbf{A} - \boldsymbol{\lambda}), \quad (22)$$

which implies Eq. (13) for the marginal probability distribution $P(\mathbf{X}; t) = \int d\mathbf{u} p(\mathbf{X}, \mathbf{u}; t)$ by using large-deviation theory.^{21,23,26} The theorem (13) extends previous relations^{35,39–41} by including the chemical fluctuations, which are essential to obtain all of the contributions to the entropy production and prove its non-negativity (12) by Jensen's inequality $\langle \exp x \rangle \geq \exp \langle x \rangle$. Figure 1 shows that the mechanochemical fluctuation theorem is satisfied. The fluctuation theorem is also valid in the nonlinear regime away from equilibrium for reactions more complicated than those considered here.^{22,26}

Suppose that the particle is subjected to an external force in the z -direction $\mathbf{F}_{\text{ext}} = (0, 0, F)$, as well as to the external magnetic field $\mathbf{B} = (0, 0, B)$ 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 relation⁴⁰ for the displacement along the z -direction

$$\frac{\mathcal{P}(z; t)}{\mathcal{P}(-z; t)} \approx \exp\left(\frac{F_{\text{eff}} z}{k_B T_{\text{eff}}}\right), \quad (23)$$

which is expressed in terms of an effective force $F_{\text{eff}} = F + F_d \langle u_z \rangle$ resulting from the external and diffusiophoretic forces, and the effective temperature $T_{\text{eff}} = T \left[1 + (V_d^2/D) \int_0^\infty C_{zz}(t) dt \right]$, where $C_{zz}(t) \equiv \langle [u_z(0) - \langle u_z \rangle][u_z(t) - \langle u_z \rangle] \rangle$ 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 $D_{\text{eff}} = D + V_d^2/(6D_{\text{rot}})$.⁹

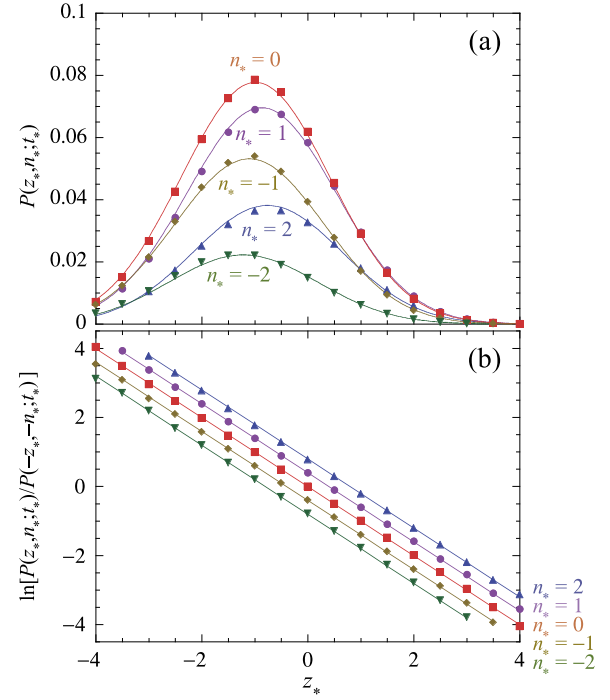


FIG. 1. Janus particle subjected to an external force and magnetic field oriented in the z -direction. (a) Probability density $P(z_*, n_*, t_*)$ with $n_* = n \sqrt{D_{\text{rot}}/D_{\text{rxn}}} = 2, 1, 0, -1, -2$ versus the rescaled displacement $z_* = z \sqrt{D_{\text{rot}}/D}$ at the rescaled time $t_* = D_{\text{rot}} t = 1$ for the parameter values $p = \beta \mu B = 1$, $f = \beta F \sqrt{D/D_{\text{rot}}} = -1$, $w = W_{\text{rxn}}/\sqrt{D_{\text{rxn}} D_{\text{rot}}} = 0.4$, and $c = \chi \sqrt{D_{\text{rxn}}/D} = 0.4$. (b) Verification of the mechanochemical fluctuation relation (13) in the same conditions. The probability ratio is calculated if $P(z_*, n_*, t_*)$ and $P(-z_*, -n_*, t_*)$ are larger than 10^{-4} . The dots are the results of a numerical simulation with an ensemble of 10^7 trajectories and an integration with the time step $dt_* = 10^{-3}$, using the method described in the Appendix. The lines depict the theoretical expectations.

More generally, the effects of mechanochemical coupling are described by Eq. (13). A key point is that the fluctuation theorem (13) would not hold without the reciprocal term due to the diffusiophoretic coupling χ in Eq. (7). A most important consequence of this term is that the reaction rate depends on the external force. In the presence of an 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 $F_{\text{stall}} = -F_d \langle u_z \rangle$ and zero. For other external force values, the motor will move in the same direction as the applied force. Since the reaction rate depends on the applied force, in the linear regime close to equilibrium, the rate can be reversed if an external force is exerted in a direction opposite to self-propulsion and satisfies $F < F_0 = -W_{\text{rxn}}/(\beta \chi D_{\text{rxn}} \langle u_z \rangle)$ (Fig. 2). In this case, the rate of fuel consumption becomes negative in Eq. (7), meaning that fuel is synthesized from product. The thermodynamic efficiency of synthesis $\eta_c \equiv -A_{\text{rxn}} \langle \dot{n} \rangle / (\beta F \langle \dot{z} \rangle)$ ¹⁴ can reach the maximum value $\eta_c^{(\text{max})} = (1 - \sqrt{1 - q^2}) / (1 + \sqrt{1 - q^2}) = 0.25 q^2 + O(q^4)$ with $-1 \leq q \equiv \chi \langle u_z \rangle \sqrt{D_{\text{rxn}}/D} \leq +1$. Therefore, the larger the diffusiophoretic coupling coefficient χ , the larger the efficiency is.

It should be possible to verify that the reaction rate of diffusiophoretic motors depends on the force applied to a motor oriented by a torque and also that a counter force of sufficient magnitude could yield the conversion of product to fuel. In

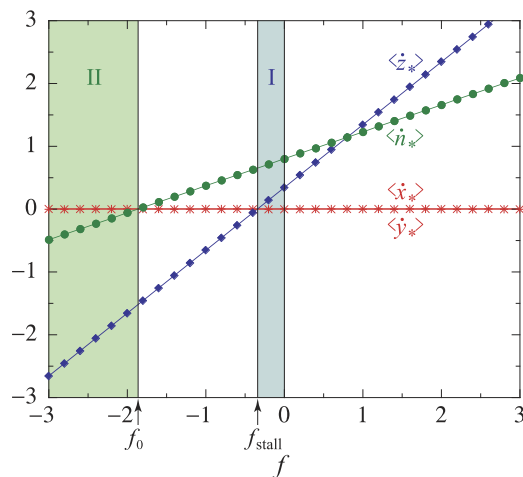


FIG. 2. Janus particle subjected to an external force and magnetic field oriented in the z -direction. The mean values of the fluctuating rescaled velocities $\dot{\mathbf{r}}_* = \dot{\mathbf{r}}/\sqrt{DD_{\text{rot}}}$ and rate $\dot{n}_* = \dot{n}/\sqrt{D_{\text{rxn}}D_{\text{rot}}}$ versus the rescaled magnitude of the external force $f = \beta F\sqrt{D/D_{\text{rot}}}$ for the parameter values $p = \beta\mu B = 2$, $w = W_{\text{rxn}}/\sqrt{D_{\text{rxn}}D_{\text{rot}}} = 0.8$, and $c = \chi\sqrt{D_{\text{rxn}}/D} = 0.8$. The dots show the results of a numerical simulation with a statistics of 10^5 trajectories integrated over the time interval $t_* = 10$, using the method described in the Appendix. f_{stall} denotes the rescaled stall force and f_0 denotes 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.

order to observe the conversion of product to fuel as a result of an applied force by the mechanism described above, it is important that the system remains in the linear regime where the theory applies. The extent of the deviation from the equilibrium state may be controlled by the values of $\bar{c}_A$ and $\bar{c}_B$, and these values should be chosen so that external force magnitudes needed for fuel production do not take the system out of the linear regime, otherwise additional nonlinear effects come into play in Eq. (5). Finally, again given that the system operates in the linear regime, we note that a corollary of this result is that the action of diffusiophoretic micropumps⁴² can also be reversed and fuel synthesized if a pressure of sufficient magnitude is applied to a product solution flowing through a microchannel or nanopore with part of its inner surface coated by catalyst. The possibility to modify the reaction rate with the external force is the reciprocal effect of self-propulsion (or pumping) and constitutes a principal prediction of this communication.

The previous results can be generalized to self-electrophoretic or self-thermophoretic motors, as well as to non-spherical shapes, where extra couplings are expected between translation, rotation, and reaction.

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APPENDIX: NUMERICAL METHOD

The coupled noises (8)–(11) of the overdamped Langevin Eqs. (3) and (7) can be simulated according to

$$\mathbf{V}_{\text{fl}}(t) = \sqrt{2D} \xi_1(t) \mathbf{u}_1 + \sqrt{2D} \xi_2(t) \mathbf{u}_2 + \left[\sqrt{D\lambda_+} \xi_3(t) - \varsigma \sqrt{D\lambda_-} \xi_4(t) \right] \mathbf{u}_3, \quad (\text{A1})$$

$$W_{\text{fl}}(t) = \varsigma \sqrt{D_{\text{rxn}}\lambda_+} \xi_3(t) + \sqrt{D_{\text{rxn}}\lambda_-} \xi_4(t), \quad (\text{A2})$$

in terms of the independent Gaussian white noises satisfying $\langle \xi_i(t) \rangle = 0$ and $\langle \xi_i(t) \xi_j(t') \rangle = \delta(t - t') \delta_{ij}$, the parameters $\lambda_{\pm} = 1 \pm \sqrt{\chi^2 D_{\text{rxn}}/D}$ and $\varsigma = \chi/|\chi|$, and the unit vectors $\{\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3 = \mathbf{u}\}$ attached to the frame of the Janus particle. The unit vector $\mathbf{u}_3 = \mathbf{u}$ is oriented along the particle axis pointing from the inactive towards the catalytic hemisphere, while $\mathbf{u}_1$ and $\mathbf{u}_2$ are perpendicular to the axis.

Besides, the rotational motion is simulated by the method of quaternions^{30,31} and the fluctuating torque $\mathbf{T}_{\text{fl}}(t) = \sqrt{2\gamma_{\text{rot}}k_B T} \boldsymbol{\xi}_{\text{rot}}(t)$ is determined by three other independent Gaussian noises such that $\langle \boldsymbol{\xi}_{\text{rot}}(t) \rangle = 0$ and $\langle \boldsymbol{\xi}_{\text{rot}}(t) \otimes \boldsymbol{\xi}_{\text{rot}}(t') \rangle = \delta(t - t')$.

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