FROM SINGLE ACTIVE PARTICLES TO ACTIVE MATTER

Pierre GASPARD
Center for Nonlinear Phenomena and Complex Systems
Université Libre de Bruxelles, Brussels, Belgium

with

Raymond KAPRAL
Chemical Physics Theory Group, Department of Chemistry
University of Toronto, Ontario, Canada

INTRODUCTION

1. **STOCHASTIC MOTION OF A SINGLE ACTIVE PARTICLE**
2. **COLLECTIVE DYNAMICS OF MANY ACTIVE PARTICLES**

Collective behavior of particles in fluids,
Institut Henri Poincaré, Paris, 14-17 December 2020

COLLECTIVE DYNAMICS IN COMPLEX SYSTEMS

Traffic on a highway: Spontaneous jam in a dense traffic

I. Prigogine & F. C. Andrews, *A Boltzmann-like approach for traffic flow*, Operations Res. **8** (1960) 789

D. Helbing, *Traffic and related self-driven many-particle systems*, Rev. Mod. Phys. **73** (2001) 1067

Collective dynamics of social insects (ants): Symmetry breaking phenomenon emerging from the interaction between the ants and their pheromones

R. Beckers, J.-L. Deneubourg & S. Goss, J. Theor. Biology **159** (1992) 397

Collective dynamics of birds: Flocks of starlings

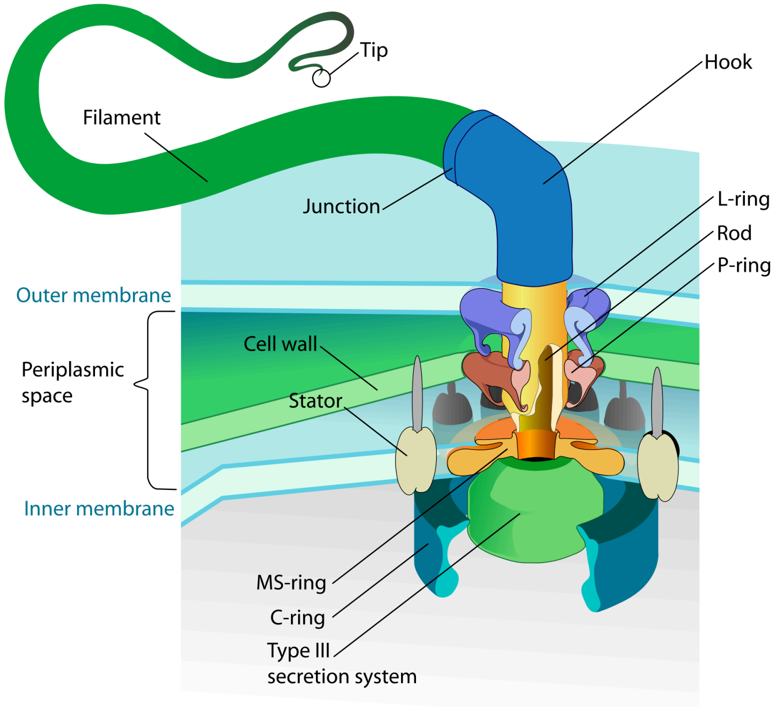
M. Ballerini et al., Proc. Natl. Acad. Sci. USA **105** (2008) 1232

Collective dynamics of fishes: Fish schools

T. Vicsek & A. Zafeiris, *Collective motion*, Phys. Rep. **517** (2012) 1

SWIMMING MICROORGANISMS

PROKARYOTES
rotating flagellum



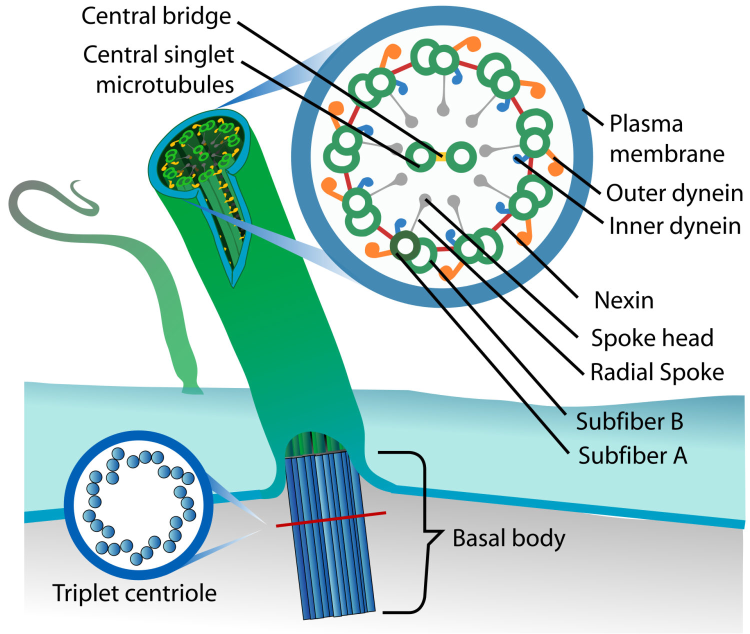
Wikipedia

Escherichia coli bacteria (1-2 μm)

with rotating flagella

Chemotaxis

EUKARYOTES
undulating cilium



spermatozoa (5+50 μm)

green alga (10 μm)

paramecium (300 μm)

with undulating cilia

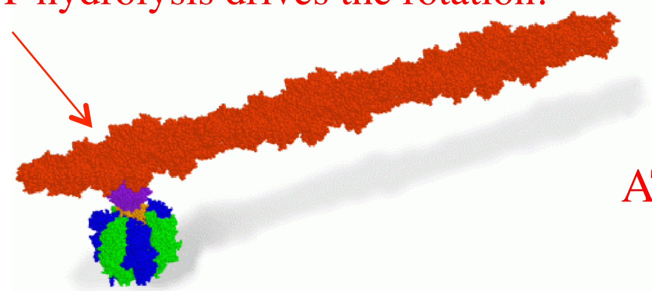
E. E. Riley, D. Das & E. Lauga, Sci. Rep. **8** (2018) 10728

BIOMOLECULAR MOTORS & PROCESSORS

Rotary motor: F_1-ATPase + filament/bead

K. Kinosita and coworkers (2001,2004)
Itoh et al., Nature **427** (2004) 465

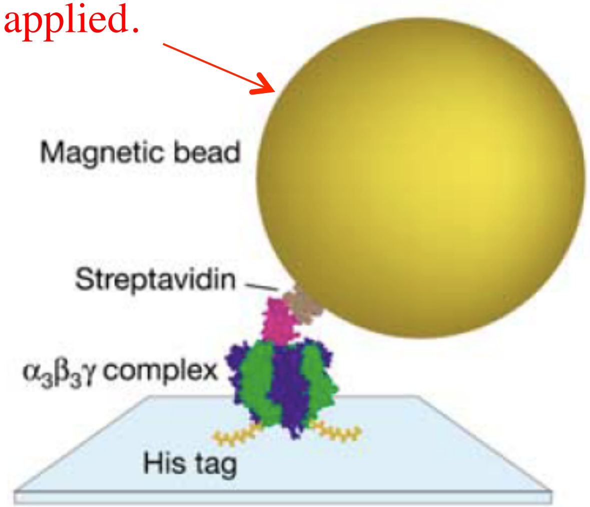
ATP hydrolysis drives the rotation.



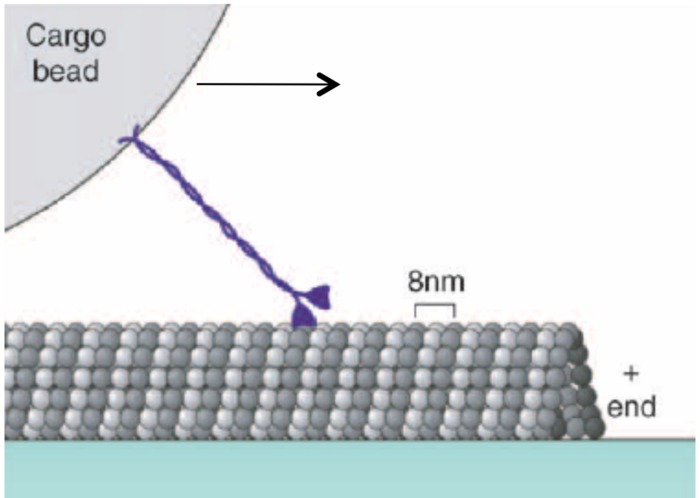
T = 300 K
power = 10^{-18} Watt
diameter = 10 nanometers

ATP hydrolysis/synthesis is coupled to mechanical motion/force.

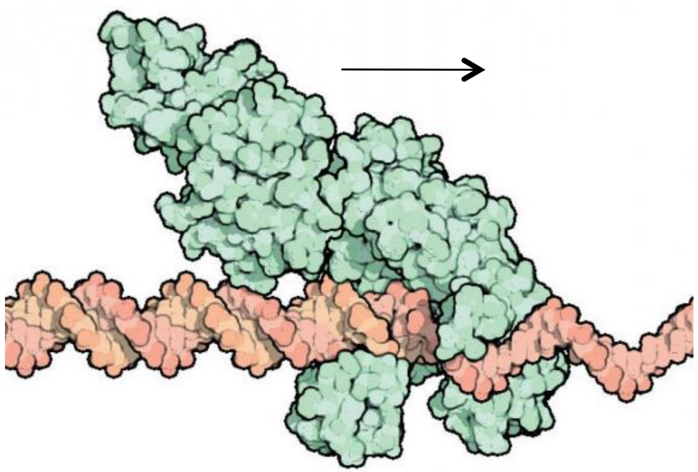
A mechanical force is also applied.



Linear motor: kinesin-microtubule



Information processor: DNA polymerase



Wikipedia

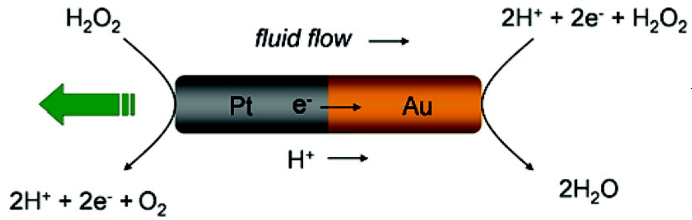
SYNTHETIC ACTIVE PARTICLES

Electrodiffusiophoresis or diffusiophoresis

W. F. Paxton et al., JACS **126** (2004) 13424
S. Fournier-Bidoz et al., Chem. Commun. (2005) 441

Fuel = hydrogen peroxide *Catalyst = platinum*

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2 \qquad V_{sd} \approx 10\ \mu m/s$$



Wikipedia

L. F. Valadares et al., Small **6** (2010) 565
J. G. Gibbs, N. A. Fragnito & Y. P. Zhao, Appl. Phys. Lett. **97** (2010) 253107
L. Baraban et al., ACS Nano **6** (2012) 3383

W. Gao, A. Pei, R. F. Dong & J. Wang, JACS **136** (2014) 2276

Fuel = hydrazine *Catalyst = iridium*

$$N_2H_4 \rightarrow N_2 + 2\ H_2$$
$$3\ N_2H_4 \rightarrow N_2 + 4\ NH_3 \qquad V_{sd} \approx 20\ \mu m/s$$

S. Sanchez, L. Soler & J. Katuri, Angew. Chem. Int. Ed. **54** (2015) 1414

Hollow silica micromotors functionalized by enzymes

X. Arqué et al., Nat. Commun. **10** (2019) 2826

Fuel = urea *Catalyst = enzyme = urease*

$$CO(NH_2)_2 + H_2O \rightarrow 2\ NH_3 + CO_2$$

enhanced diffusion due to self-propulsion

COLLECTIVE DYNAMICS OF SYNTHETIC ACTIVE PARTICLES

Electrodiffusiophoresis or diffusiophoresis

M. Ibele, T. E. Mallouk & A. Sen,
Angew. Chem. Int. Ed. **48** (2009) 3308

Cluster formation:

active AgCl particles,
passive silica particles,
fuel = hydrogen peroxide,
UV light

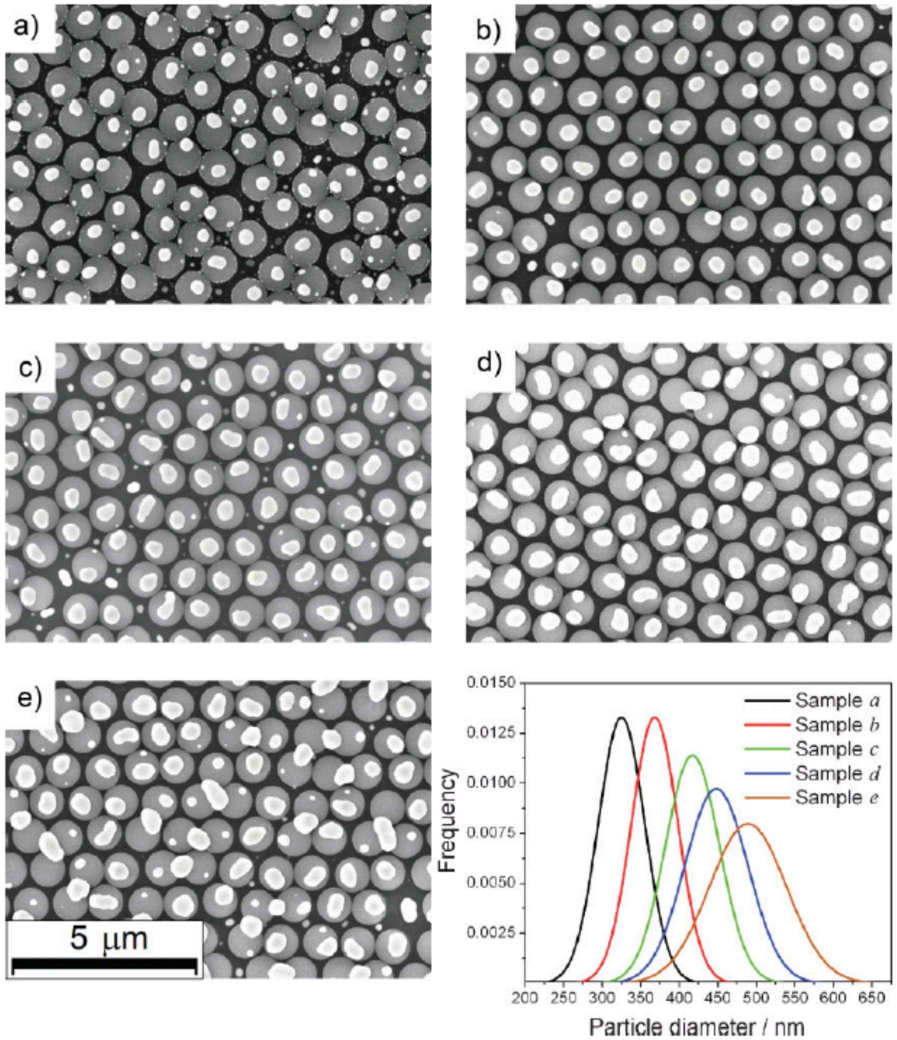
I. Buttinoni et al., Phys. Rev. Lett. **110** (2013) 238301
C. Bechinger et al., Rev. Mod. Phys. **88** (2016) 045006

Cluster formation:

active Janus particles,
diffusiophoresis due to
local demixing by heating with light

SYNTHESIS OF NANOMETRIC ACTIVE PARTICLES

L. F. Valadares, Y.-G. Tao, N. S. Zacharia,
V. Kitaev, F. Galembeck, R. Kapral & G. A. Ozin,
Catalytic Nanomotors: Self-Propelled Sphere Dimers, Small **6** (2010) 565-572

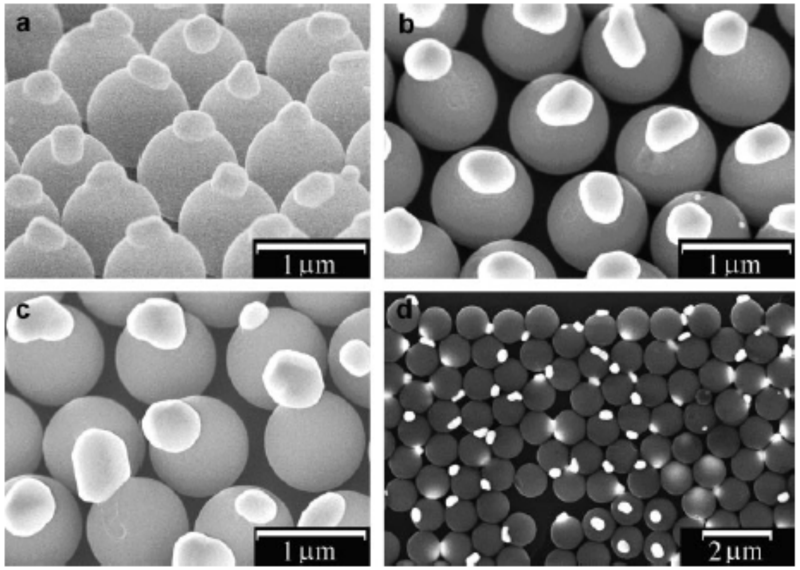


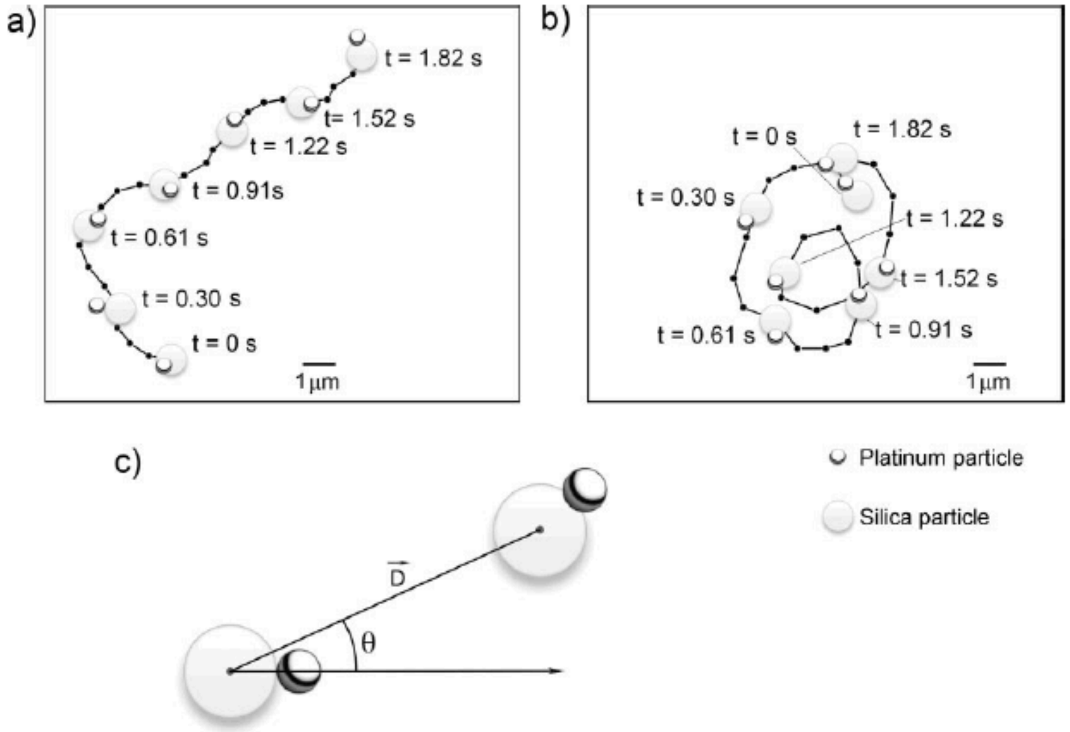
silica particles
+ thin chromium adhesion layer
+ thicker platinum catalytic layer

Sample	Pt layer thickness [nm]	Pt particle diameter [nm]	Percentage of sphere dimers in the sample [%]	Average speed of the sphere dimers in 15% H_2O_2 solution [$\mu m\ s^{-1}$]
a	25	325 ± 30	75.1	2.5 ± 0.2
b	40	368 ± 30	85.3	3.5 ± 1.4
c	55	417 ± 35	71.2	5.1 ± 1.7
d	70	448 ± 41	80.9	6.0 ± 4.0
e	85	489 ± 50	42.2	5.6 ± 3.7

ACTIVE PARTICLES: LOCALLY CONSUMING ENERGY

L. F. Valadares, Y.-G. Tao, N. S. Zacharia, V. Kitaev, F. Galembeck, R. Kapral & G. A. Ozin, *Catalytic Nanomotors: Self-Propelled Sphere Dimers*, Small **6** (2010) 565-572





silica particle + platinum dot

reaction on platinum:

$$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$$

15% H_2O_2 solution:

$$V_{sd} = 2.5 - 6\ \mu m/s$$

Observations:

- random changes of orientation ($t > t_{rot}$)
- random walk with enhanced diffusion

PROPULSION MECHANISMS

High Reynolds numbers: Re = $VL/\nu \gg 1$: turbulent flow

- fishes in water (herring Re = $3\ 10^5$)
- birds in air (sparrow Re = $2\ 10^5$)

Low Reynolds numbers: Re = $VL/\nu \ll 1$: laminar flow

scallop no-go theorem:

Propulsion cannot be generated by
the reciprocal motion of the shape (Purcell 1977)

C. Bechinger et al.,
Rev. Mod. Phys.
88 (2016) 045006

- Active particles changing their shape:
  - rotary flagella for swimming bacteria
  - cilia for swimming eukaryotes

- Rigid active particles:
  - diffusiophoresis, electrodiffusiophoresis, thermophoresis

- Tensioactive mechanisms: (Marangoni effects: gradients in surface tension)
  - changes in surface tension by varying reactive concentration or temperature
  - changes in adhesion (amoeba)

SEVERAL LEVELS OF DESCRIPTION FOR A GIVEN PHENOMENON

Macroscopic level: (centimetric)
Deterministic partial differential equations
for the density and polarization of active particles,
the fluid velocity, and the concentrations of fuel and product reacting molecules.

⬆

Mesoscopic level: (micrometric)
Stochastic processes for the random motion of active particles
(Langevin stochastic equations) and
for the fluctuating chemohydrodynamics of the solution surrounding the particles
(stochastic partial differential equations with suitable boundary conditions).

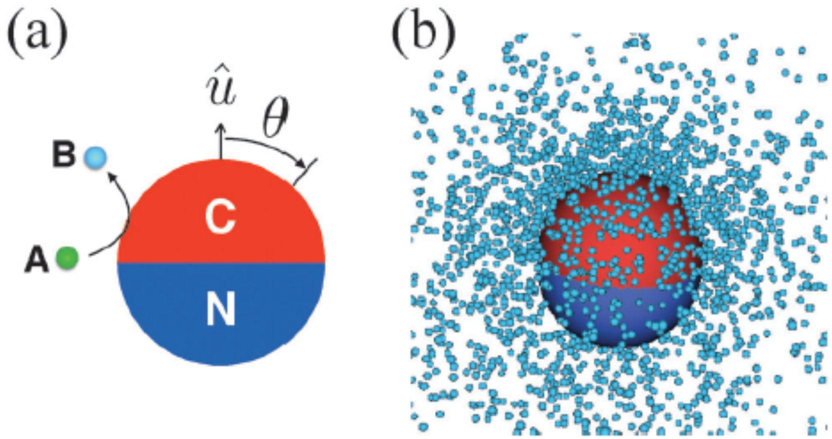
⬆

Microscopic level: (subnanometric)
Hamiltonian dynamics of atoms and molecules composing the fluid
and the active particles ($\sim 10^{23}$ coupled ordinary differential equations).

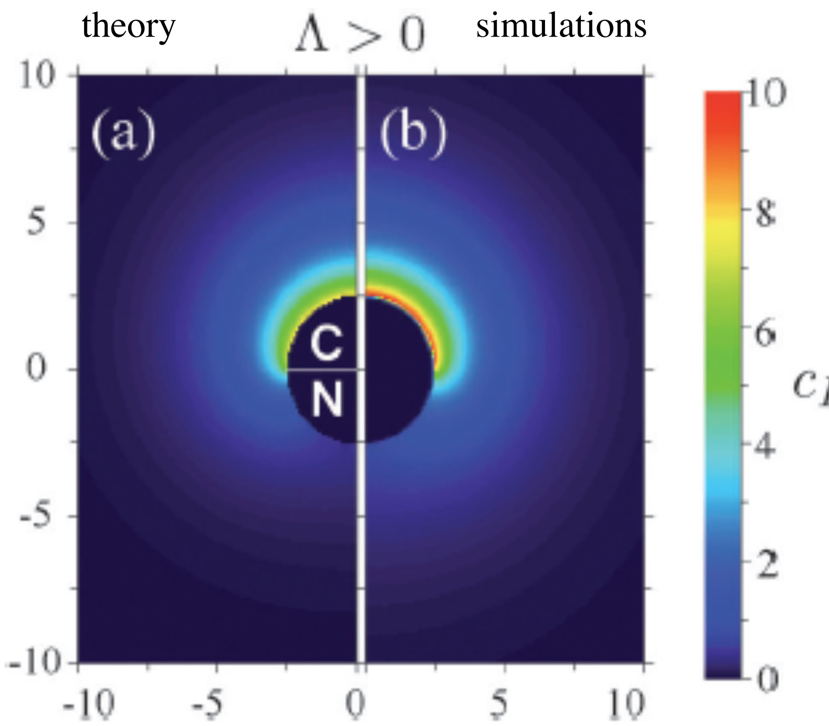
1. STOCHASTIC MOTION OF A SINGLE ACTIVE PARTICLE

PROPULSION BY SELF-DIFFUSIOPHORESIS

M.-J. Huang, J. Schofield & R. Kapral,
A microscopic model for chemically-powered Janus motors, Soft Matter **12** (2016) 5581



Janus particle with catalytic (C)
and non-catalytic (N) hemispheres



product concentration field $c_B(r,\theta)$

Navier-Stokes equation modified by the
interaction potentials u_A and u_B of reactant A and product B with the Janus particle:

$$\rho\left(\partial_t \mathbf{v} + \mathbf{v}\cdot\nabla\mathbf{v}\right) = -\nabla P + \eta\nabla^2\mathbf{v} - c_A\nabla u_A - c_B\nabla u_B$$

inducing a velocity slip

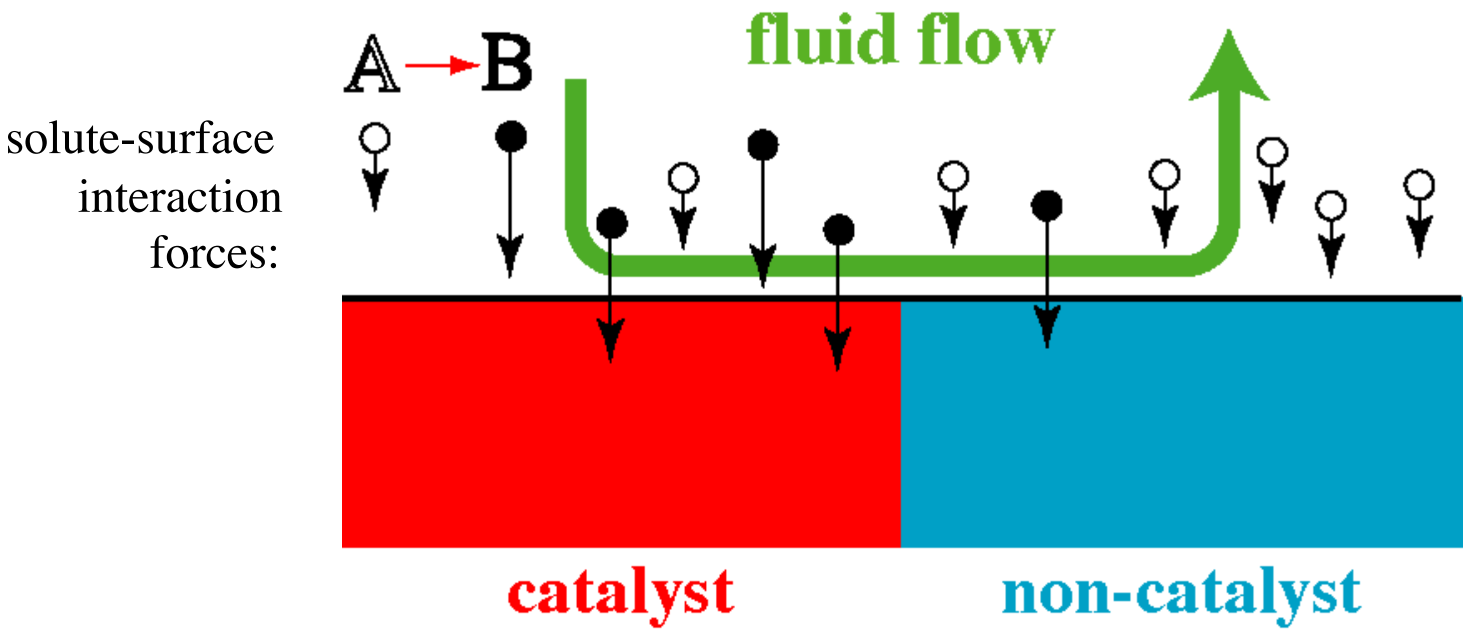
THE MOLECULAR MECHANICS OF DIFFUSIOPHORESIS

Active nonequilibrium process in locally generated gradients

Navier-Stokes equation modified by the interaction potentials u_{A} and u_{B} of reactant A and product B with the surface:

$$\rho\left(\partial_t \mathbf{v} + \mathbf{v}\cdot\nabla\mathbf{v}\right) = -\nabla P + \eta\nabla^2\mathbf{v} - c_{\mathrm{A}}\nabla u_{\mathrm{A}} - c_{\mathrm{B}}\nabla u_{\mathrm{B}}$$

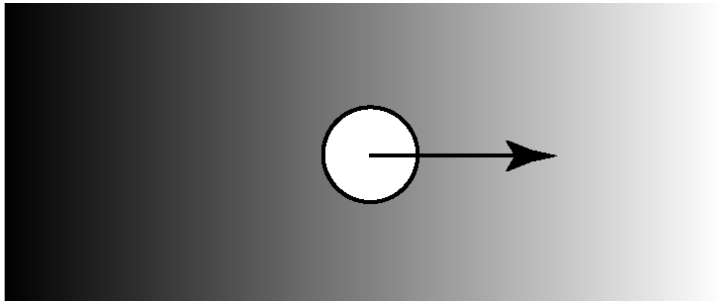
- Solutes A and B in solution;
- Suppose that A-surface interaction < B-surface interaction;
- The fluid-surface force is larger where B is more concentrated;
- A fluid flow is generated from the concentration gradient;
- Hence, the fluid flow and the velocity slip.



DIFFUSIOPHORESIS & THERMOPHORESIS

Passive nonequilibrium processes in externally driven gradients

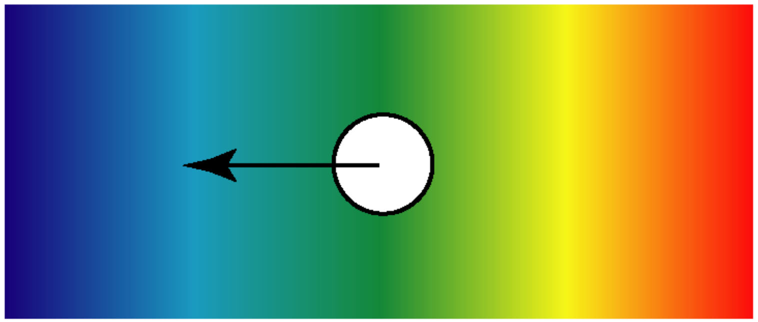
DIFFUSIOPHORESIS: Motion of a spherical particle in a solute gradient ∇c_k

$c_{k,\mathrm{low}}$  $c_{k,\mathrm{high}}$

diffusiophoretic velocity: $\mathbf{V}_\mathrm{d} = b_k \nabla c_k$ $b_k =$ diffusiophoretic coefficient

(stick boundary conditions) (zero molecular diffusivity in solid)

THERMOPHORESIS: Motion of a spherical particle in a temperature gradient ∇T

T_cold  T_hot

thermophoretic velocity: $\mathbf{V}_\mathrm{th} = b_q \dfrac{2\kappa_\mathrm{f}}{2\kappa_\mathrm{f} + \kappa_\mathrm{s}} \nabla T$

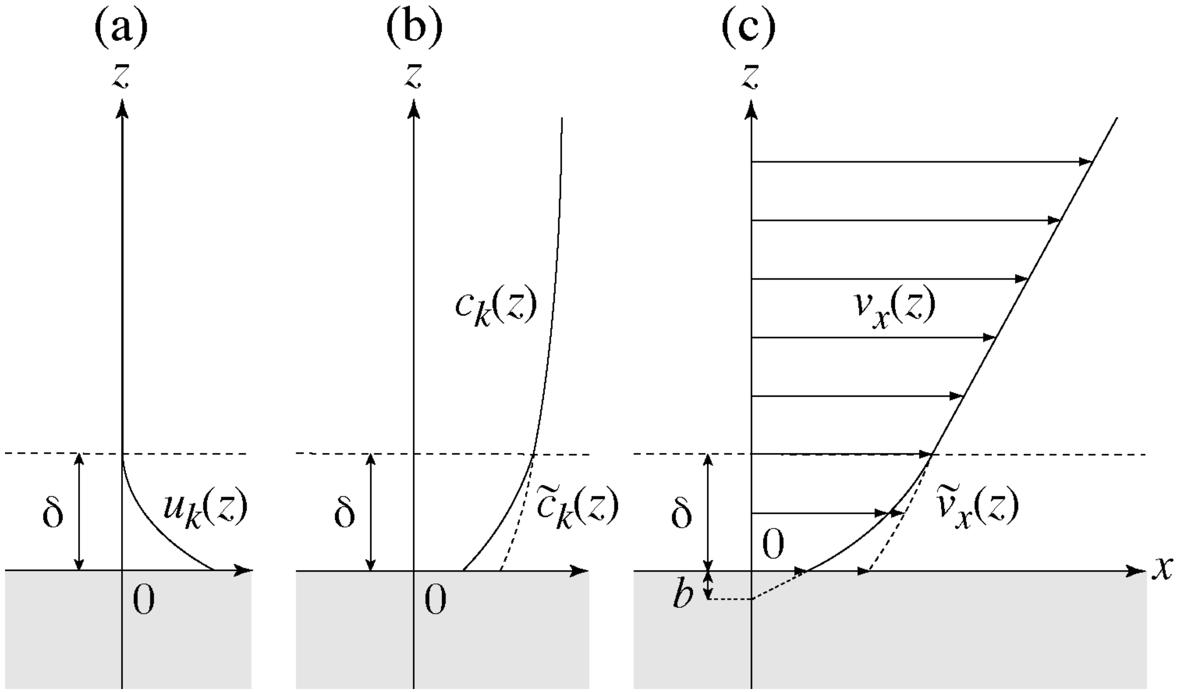
(stick boundary conditions)

$b_q =$ thermophoretic coefficient

$\kappa_\mathrm{f}, \kappa_\mathrm{s} =$ fluid & solid heat conductivities

thermodiffusion or Soret effect: $\mathbf{J}_\mathrm{diff} = -D\left(\nabla n + nS_T \nabla T\right)$

DIFFUSIOPHORESIS IN THE THIN-LAYER APPROXIMATION



slip length:

$$b = \frac{\eta}{\lambda}$$

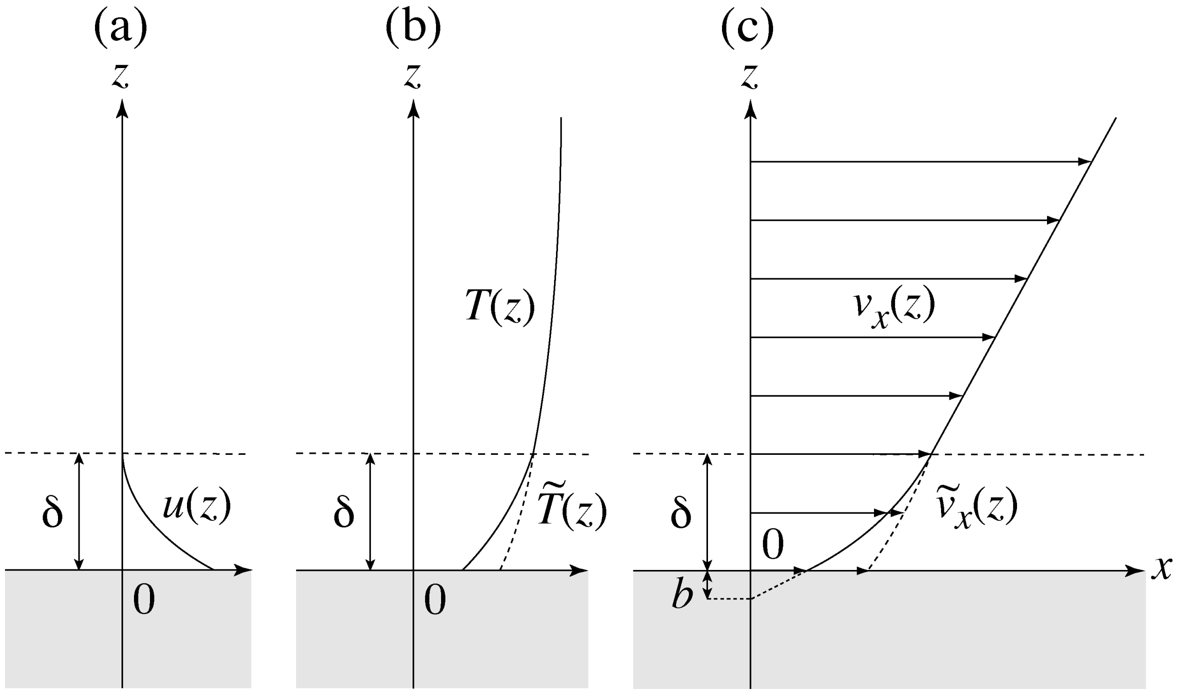
Within the boundary layer, the Navier-Stokes and diffusion equations should include the solute-wall interaction potentials u_k. Matching the concentration and velocity fields beyond the boundary layer, we get the ***diffusiophoretic coefficients***:

$$b_k = \frac{k_B T}{\eta}\left(K_k^{(1)} + b K_k^{(0)}\right) \qquad \text{with} \qquad K_k^{(n)} \equiv \int_0^{\delta} dz\, z^n \left[e^{-\beta u_k(z)} - 1\right]$$

The case $b = 0$: J. L. Anderson, Annu. Rev. Fluid Mech. **21** (1989) 61

The case $b \neq 0$: A. Ajdari & L. Bocquet, Phys. Rev. Lett. **96** (2006) 186102

THERMOPHORESIS IN THE THIN-LAYER APPROXIMATION



slip length:

$$b = \frac{\eta}{\lambda}$$

Within the boundary layer, the Navier-Stokes and heat equations should include the fluid-wall interaction potential u. Matching the temperature and velocity fields beyond the boundary layer, we get the ***thermophoretic coefficient***:

$$b_q = \frac{1}{\eta T}\left(H^{(1)} + bH^{(0)}\right) \qquad \text{with} \qquad H^{(n)} \equiv \int_0^\delta dz\, z^n\left[h(z) - h_{\text{bulk}}\right]$$

excess enthalpy density

The case $b = 0$: R. Ganti, Y. Liu & D. Frenkel, Phys. Rev. Lett. **119** (2017) 038002
The case $b \neq 0$: L. Fu, S. Merabia & L. Joly, Phys. Rev. Lett. **119** (2017) 214501

LINEAR REGIME CLOSE TO EQUILIBRIUM

current-affinity linear coupling, including the fluctuations: $J_\alpha = \sum_\beta L_{\alpha\beta} A_\beta + \delta J_\alpha$

fluctuations = Gaussian white noise processes: $\langle \delta J_\alpha(t) \rangle = 0$

fluctuation-dissipation theorem $\langle \delta J_\alpha(t) \delta J_\beta(t') \rangle = (L_{\alpha\beta} + L_{\beta\alpha}) \delta(t - t')$

entropy production rate: $\frac{1}{k_B} \frac{d_i S}{dt} = \sum_\alpha A_\alpha \langle J_\alpha \rangle = \sum_\alpha L_{\alpha\beta} A_\alpha A_\beta \geq 0$

Onsager-Casimir reciprocal relations: ***microreversibility***

$L_{\alpha\beta} = \varepsilon_\alpha \varepsilon_\beta L_{\beta\alpha}$ where $\varepsilon_\alpha = \pm 1$ when A_α is even or odd under time reversal.

L. Onsager, Phys. Rev. **37** (1931) 405: **38** (1931) 2265
H. B. G. Casimir, Rev. Mod. Phys. **17** (1945) 343

NONEQUILIBRIUM THERMODYNAMICS IN FLUIDS

local balance equation of entropy density s: $\partial_t s + \nabla \cdot \mathbf{j}_s = \sigma_s \geq 0$

balance equation of total entropy: $\frac{dS}{dt} = \int_V \partial_t s \, dV = -\int_{\partial V} \mathbf{j}_s \cdot d\Sigma + \int_V \sigma_s \, dV = \frac{d_e S}{dt} + \frac{d_i S}{dt}$

entropy production rate density: $\sigma_s = \sum_\alpha A_\alpha J_\alpha \geq 0$

entropy production rate: $\frac{d_i S}{dt} \geq 0$

2nd law

Onsager coupling: $J_\alpha = \sum_\beta L_{\alpha\beta} A_\beta$

irreversible process α	affinity A_α	current J_α	space	time
shear viscosity	$\mathring{\mathbf{A}}_\mathrm{p} = -\frac{1}{T}\left[(\boldsymbol{\nabla}\mathbf{v})^{\mathrm{sym}} - \frac{1}{3}\boldsymbol{\nabla}\cdot\mathbf{v}\right]$	$\mathring{\mathbf{J}}_\mathrm{p} = \mathring{\mathbf{\Pi}}$	tensor	odd
dilatational viscosity	$A_\mathrm{p} = -\frac{1}{T}\boldsymbol{\nabla}\cdot\mathbf{v}$	$J_\mathrm{p} = \Pi$	scalar	odd
reaction r	$A_r = -\frac{1}{T}\sum_k \mu_k \nu_{kr}$	$J_r = w_r$	scalar	even
heat conductivity	$\mathbf{A}_q = \boldsymbol{\nabla}\frac{1}{T}$	$\mathbf{J}_q$	vector	even
diffusion of species k	$\mathbf{A}_k = -\boldsymbol{\nabla}\frac{\mu_k}{T}$	$\mathbf{J}_k$	vector	even

I. Prigogine, Etude thermodynamique des phénomènes irréversibles (Desoer, Liège, 1947)

S. R. de Groot & P. Mazur, Non-Equilibrium Thermodynamics (Dover, NY, 1984)

INTERFACIAL NONEQUILIBRIUM THERMODYNAMICS

density decomposition between the two phases ± and the interface s: $x = x^+\theta^+ + x^s\delta^s + x^-\theta^-$

local balance equations of x at the interface s: playing the role of boundary conditions for $x^\pm$

$$\partial_t x^s + \nabla\cdot\left(x^s\mathbf{v}^s + \mathbf{J}_x^s\right) = \sigma_x^s - \mathbf{n}\cdot\left[\mathbf{J}_x^+ + x^+\left(\mathbf{v}^+ - \mathbf{v}^s\right)\right] + \mathbf{n}\cdot\left[\mathbf{J}_x^- + x^-\left(\mathbf{v}^- - \mathbf{v}^s\right)\right] \qquad \mathbf{n}\cdot\mathbf{J}_x^s = 0$$

interfacial entropy production rate density: $\sigma_s^s = \sum_\alpha A_\alpha^s J_\alpha^s$

Onsager coupling: $J_\alpha^s = \sum_\beta L_{\alpha\beta}^s A_\beta^s$

$$\tilde{\Pi} = \Pi + \tfrac{\rho}{2}(\mathbf{v}-\mathbf{v}^s)^2\mathbf{1}$$
$$\tilde{\mathbf{J}}_q = \tilde{\mathbf{J}}_q + h(\mathbf{v}-\mathbf{v}^s)$$
$$\tilde{\mathbf{J}}_k = \tilde{\mathbf{J}}_k + c_k(\mathbf{v}-\mathbf{v}^s)$$

irreversible process α	affinity A_α	current J_α	space	time
shear interfacial viscosity	$\mathring{\mathbf{A}}_{\mathrm{p}}^{\mathrm{s}} = -\frac{1}{T^{\mathrm{s}}}\mathbf{1}_\perp\cdot\left[(\boldsymbol{\nabla}\mathbf{v}^{\mathrm{s}})^{\mathrm{sym}} - \frac{1}{2}\boldsymbol{\nabla}\cdot\mathbf{v}^{\mathrm{s}}\right]\cdot\mathbf{1}_\perp$	$\mathring{\mathbf{J}}_{\mathrm{p}}^{\mathrm{s}} = \mathring{\mathbf{\Pi}}^{\mathrm{s}}$	tensor	odd
dilatational interfacial viscosity	$A_{\mathrm{p}}^{\mathrm{s}} = -\frac{1}{T^{\mathrm{s}}}\boldsymbol{\nabla}\cdot\mathbf{v}^{\mathrm{s}}$	$J_{\mathrm{p}}^{\mathrm{s}} = \Pi^{\mathrm{s}}$	scalar	odd
interfacial reaction r	$A_r^{\mathrm{s}} = -\frac{1}{T^{\mathrm{s}}}\sum_k \mu_k^{\mathrm{s}}\nu_{kr}$	$J_r^{\mathrm{s}} = w_r^{\mathrm{s}}$	scalar	even
heat conductivity inside interface	$\mathbf{A}_q^{\mathrm{s}} = \boldsymbol{\nabla}_\perp\frac{1}{T^{\mathrm{s}}}$	$\mathbf{J}_q^{\mathrm{s}}$	vector	even
diffusion of species k inside interface	$\mathbf{A}_{k\parallel}^{\mathrm{s}} = -\boldsymbol{\nabla}_\perp\frac{\mu_k^{\mathrm{s}}}{T^{\mathrm{s}}}$	$\mathbf{J}_{k\parallel}^{\mathrm{s}}$	vector	even
interfacial slippage	$\mathbf{A}_{\mathrm{v}\perp}^{\mathrm{s}} = -\frac{1}{T^{\mathrm{s}}}(\mathbf{v}^+ - \mathbf{v}^-)$	$\mathbf{J}_{\mathrm{v}\perp}^{\mathrm{s}} = \frac{1}{2}\mathbf{n}\cdot\left(\tilde{\mathbf{\Pi}}^+ + \tilde{\mathbf{\Pi}}^-\right)$	vector	odd
interfacial displacement	$\mathbf{A}_{\mathrm{v}\top}^{\mathrm{s}} = -\frac{1}{T^{\mathrm{s}}}\left(\frac{\mathbf{v}^+ + \mathbf{v}^-}{2} - \mathbf{v}^{\mathrm{s}}\right)$	$\mathbf{J}_{\mathrm{v}\top}^{\mathrm{s}} = \mathbf{n}\cdot\left(\tilde{\mathbf{\Pi}}^+ - \tilde{\mathbf{\Pi}}^-\right)$	vector	odd
heat conductivity across interface	$A_{q\perp}^{\mathrm{s}} = \frac{1}{T^+} - \frac{1}{T^-}$	$J_{q\perp}^{\mathrm{s}} = \frac{1}{2}\mathbf{n}\cdot\left(\tilde{\mathbf{J}}_q^+ + \tilde{\mathbf{J}}_q^-\right)$	scalar	even
heat conductivity to interface	$A_{q\top}^{\mathrm{s}} = \frac{1}{2}\left(\frac{1}{T^+} + \frac{1}{T^-}\right) - \frac{1}{T^{\mathrm{s}}}$	$J_{q\top}^{\mathrm{s}} = \mathbf{n}\cdot\left(\tilde{\mathbf{J}}_q^+ - \tilde{\mathbf{J}}_q^-\right)$	scalar	even
transport of species k across interface	$A_{k\perp}^{\mathrm{s}} = -\frac{\mu_k^+}{T^+} + \frac{\mu_k^-}{T^-}$	$J_{k\perp}^{\mathrm{s}} = \frac{1}{2}\mathbf{n}\cdot\left(\tilde{\mathbf{J}}_k^+ + \tilde{\mathbf{J}}_k^-\right)$	scalar	even
transport of species k to interface	$A_{k\top}^{\mathrm{s}} = -\frac{1}{2}\left(\frac{\mu_k^+}{T^+} + \frac{\mu_k^-}{T^-}\right) + \frac{\mu_k^{\mathrm{s}}}{T^{\mathrm{s}}}$	$J_{k\top}^{\mathrm{s}} = \mathbf{n}\cdot\left(\tilde{\mathbf{J}}_k^+ - \tilde{\mathbf{J}}_k^-\right)$	scalar	even

D. Bedeaux, A. M. Albano & P. Mazur, Physica A **82** (1976) 438

BROWNIAN MOTION & FLUCTUATING HYDRODYNAMICS

The Langevin equation of Brownian motion can be deduced from the fluctuating hydrodynamics: *deduction of long-time tails*.

R. Zwanzig & M. Bixon, Phys. Rev. A **2** (1970) 2005
E. H. Hauge & A. Martin-Löf, J. Stat. Phys. **7** (1973) 259
D. Bedeaux & P. Mazur, Physica A **76** (1974) 247
J. W. Dufty, Phys. Fluids **17** (1974) 328

$$m\frac{d\mathbf{V}}{dt} = -\int_{S(t)} \mathbf{P}(\mathbf{r},t)\cdot \mathbf{n}\, d\Sigma + \mathbf{F}_{\text{ext}} \qquad \mathbf{I}\cdot\frac{d\Omega}{dt} = -\int_{S(t)} \Delta\mathbf{r}\times\mathbf{P}(\mathbf{r},t)\cdot\mathbf{n}\, d\Sigma + \mathbf{T}_{\text{ext}}$$

Fluctuating hydrodynamics (incompressible fluid): η = shear viscosity

$$\rho\left(\partial_t\mathbf{v} + \mathbf{v}\cdot\nabla\mathbf{v}\right) = -\nabla\cdot\mathbf{P} \qquad \mathbf{P} = P\mathbf{1} - \eta\left(\nabla\mathbf{v} + \nabla\mathbf{v}^{\mathrm{T}}\right) + \pi \qquad \nabla\cdot\mathbf{v} = 0$$

noises: $\left\langle \pi_{ij}(\mathbf{r},t)\pi_{kl}(\mathbf{r}',t')\right\rangle = 2\eta k_{\mathrm{B}}T\left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}\right)\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$

Fluctuating diffusion equations:

$$\partial_t c_k + \nabla\cdot\mathbf{j}_k = 0 \qquad \mathbf{j}_k = c_k\mathbf{v} - D_k\nabla c_k + \delta\mathbf{j}_k$$

noises: $\left\langle \delta\mathbf{j}_k(\mathbf{r},t)\otimes\delta\mathbf{j}_{k'}(\mathbf{r}',t')\right\rangle = 2D_k c_k\delta_{kk'}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')\mathbf{1}$

$\longrightarrow$ **Fluctuating chemohydrodynamics** + *boundary conditions ?*

BOUNDARY CONDITIONS

The boundary conditions are imposed at the surface of the Janus particle.
They express the surface reaction, as well as the velocity slip
due to diffusiophoresis and friction (*cf. interfacial nonequilibrium thermodynamics*).

Slip velocity due to diffusiophoresis and friction: **v** fluid velocity; **V** particle velocity

normal to the interface: **n**

$$\begin{cases} \mathbf{n}\cdot\,\mathbf{v}(\mathbf{r},t)\big|_R = \mathbf{n}\cdot\,\mathbf{V}(t) \\ \mathbf{v}_{\text{slip}} = (\mathbf{1}-\mathbf{nn})\cdot\left\{\mathbf{v}(\mathbf{r},t)-\mathbf{V}(t)-\Omega(t)\times\left[\mathbf{r}-\mathbf{R}(t)\right]\right\}_R \\ = (\mathbf{1}-\mathbf{nn})\cdot\left\{b\left[\nabla\mathbf{v}(\mathbf{r},t)+\nabla\mathbf{v}^{\text{T}}(\mathbf{r},t)\right]\cdot\,\mathbf{n}+\mathbf{v}_{\text{fl}}^{\text{s}}(\mathbf{r},t)-\sum_k b_k\nabla c_k(\mathbf{r},t)\right\}_R \end{cases}$$

slip length: $b=\dfrac{\eta}{\lambda}$ surface friction noise: $\mathbf{v}_{\text{fl}}^{\text{s}}(\mathbf{r},t)$ diffusiophoretic coefficient: b_k

Surface reaction:

$$\begin{cases} -D_{\text{A}}\mathbf{n}\cdot\,\nabla c_{\text{A}}\big|_R = -\left(\kappa_+c_{\text{A}}-\kappa_-c_{\text{B}}\right)_R+\xi_{\text{fl}}^{\text{s}}(\mathbf{r},t)-\Sigma_{\text{A}} \\ -D_{\text{B}}\mathbf{n}\cdot\,\nabla c_{\text{B}}\big|_R = +\left(\kappa_+c_{\text{A}}-\kappa_-c_{\text{B}}\right)_R-\xi_{\text{fl}}^{\text{s}}(\mathbf{r},t)-\Sigma_{\text{B}} \end{cases}$$

surface reaction noise: $\xi_{\text{fl}}^{\text{s}}(\mathbf{r},t)$

source from the excess surface density Γ_k: $\Sigma_k \equiv \partial_t\Gamma_k+\nabla_\perp\cdot\left(\Gamma_k\mathbf{v}^{\text{s}}+\mathbf{J}_k^{\text{s}}\right)$

P. Gaspard & R. Kapral, J. Chem. Phys. **148** (2018) 134104; 194114

CONCENTRATION FIELDS AROUND A JANUS PARTICLE

Spherical Janus particle:
concentration profiles
in a uniform background $\left(\bar{c}_{\rm A},\bar{c}_{\rm B}\right)$

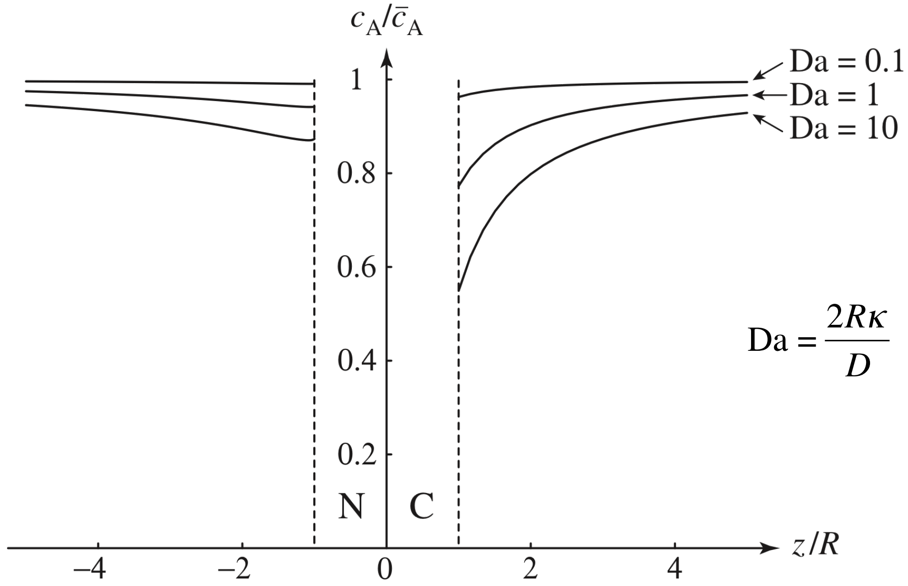
R = particle radius

$$\begin{cases} c_{\rm A}(r,\theta) = \bar{c}_{\rm A} - \dfrac{R}{D_{\rm A}}\left(\kappa_+\bar{c}_{\rm A} - \kappa_-\bar{c}_{\rm B}\right) f(r,\theta) \\ c_{\rm B}(r,\theta) = \bar{c}_{\rm B} + \dfrac{R}{D_{\rm B}}\left(\kappa_+\bar{c}_{\rm A} - \kappa_-\bar{c}_{\rm B}\right) f(r,\theta) \end{cases}$$

$$f(r,\theta) = \sum_{l=0}^{\infty} a_l P_l(\cos\theta)\left(\frac{R}{r}\right)^{l+1}$$

P_l = Legendre polynomials

Fuel concentration field $c_{\rm A}$
around a Janus particle
with the reaction A↔B
on the catalytic hemisphere C



reaction rate: $$W_{\rm rxn} = \int_{\rm catalyst} dS(\kappa_+ c_{\rm A} - \kappa_- c_{\rm B}) = \Gamma(\kappa_+\bar{c}_{\rm A} - \kappa_-\bar{c}_{\rm B}) \qquad \Gamma = 4\pi R^2 a_0$$

P. Gaspard & R. Kapral, Adv. Phys. X **4** (2019) 1602480

ASYMPTOTIC VELOCITY FIELDS

Stokes equations: $\eta \nabla^2 \mathbf{v} = \nabla P$ $\quad \nabla \cdot \mathbf{v} = 0$ $\quad$ spherical particle of radius R

- particle driven by an external force:

$$\mathbf{v} = \frac{3}{4}\frac{R}{r}\left(\mathbf{V} + \hat{\mathbf{r}}\hat{\mathbf{r}}\cdot \mathbf{V}\right) + \frac{1}{4}\left(\frac{R}{r}\right)^3 \left(\mathbf{V} - 3\hat{\mathbf{r}}\hat{\mathbf{r}}\cdot \mathbf{V}\right) \qquad \mathbf{V} = \mathbf{F}_{\text{ext}}/\gamma$$

- particle driven by diffusiophoresis:

$$\mathbf{v} = -\frac{1}{2}\left(\frac{R}{r}\right)^3 \left(\mathbf{V} - 3\hat{\mathbf{r}}\hat{\mathbf{r}}\cdot \mathbf{V}\right) \qquad \mathbf{V} = \sum_k b_k \mathbf{g}_k$$

b_k = diffusiophoretic coefficient of molecular species k

$\mathbf{g}_k$ = uniform gradient of molecular species k

- particle of axis **u** driven by self-diffusiophoresis:

$$\mathbf{v} = \frac{B_2}{2}\left(\frac{R}{r}\right)^2 \left[1 - 3(\hat{\mathbf{r}}\cdot \mathbf{u})^2\right] \hat{\mathbf{r}} + O(r^{-3}) \qquad B_2 \propto V_{\text{sd}}$$

pusher $B_2 < 0$

spermatozoon

puller $B_2 > 0$

green alga

Chamydomonas reinhardtii

E. Lauga & T. R. Powers, Rep. Prog. Phys. **72** (2009) 096601

VELOCITY FIELD AROUND A JANUS PARTICLE

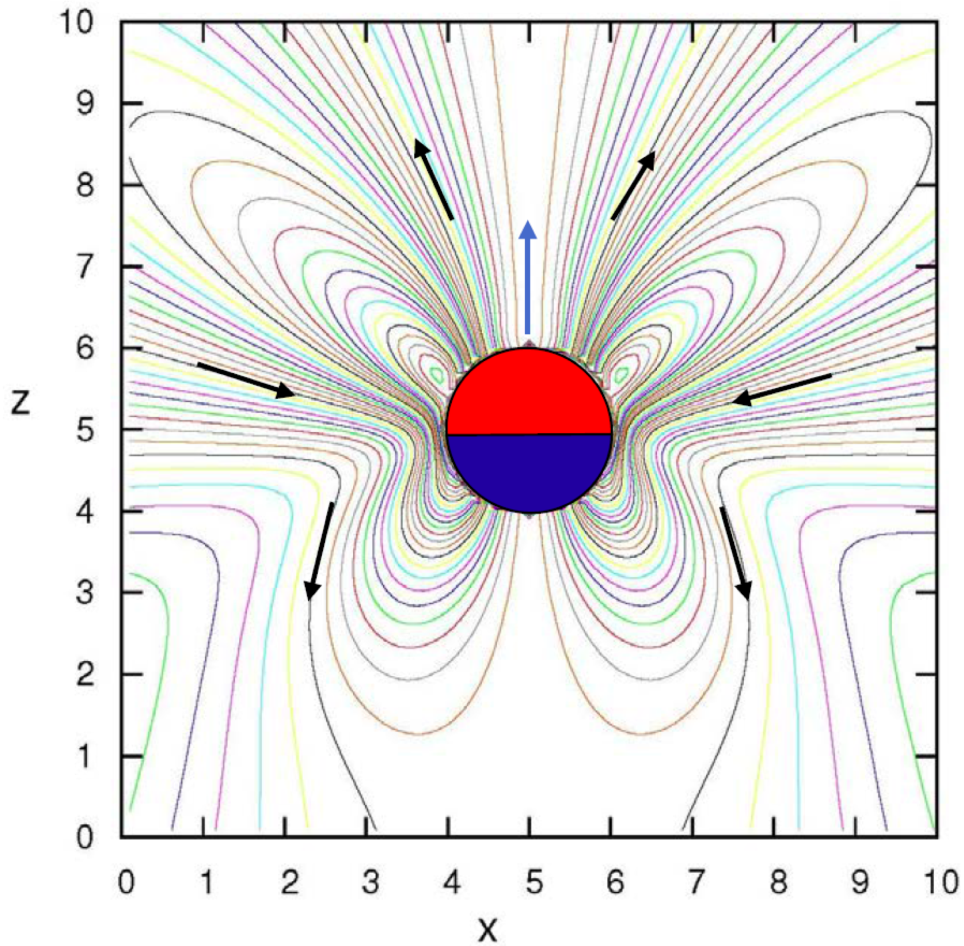
R = radius

$$\mathrm{Re} = \frac{V_{\mathrm{sd}} R}{\nu} \approx 0.013,$$

$$\mathrm{Pe} = \frac{V_{\mathrm{sd}} R}{D} \approx 0.17,$$

$$\mathrm{Da} = \frac{2R\kappa}{D} \approx 6.2$$

The Janus particle is here a **pusher**



S. Y. Reigh, M.-J. Huang, J. Schofield & R. Kapral, Phil. Trans. R. Soc. A **374** (2016) 20160140

STOCHASTIC MOTION OF THE JANUS PARTICLE

Using the method developed by D. Bedeaux & P. Mazur [Physica A **76** (1974) 247], we get in the low-frequency limit the Langevin equation:

$$m\frac{d\mathbf{V}}{dt} = -\gamma\mathbf{V} + \mathbf{F}_{\rm d} + \mathbf{F}_{\rm ext} + \mathbf{F}_{\rm fluct}(t)$$

Stokes friction coefficient with slip-length corrections: $\gamma = 6\pi\eta R\frac{1+2b/R}{1+3b/R}$

diffusiophoretic force: $\mathbf{F}_{\rm d} = \frac{6\pi\eta R}{1+3b/R}\sum_k \overline{b_k(\mathbf{1}-\mathbf{nn})\cdot\nabla c_k(r,t)}^{\rm s}$ $\qquad R$ = radius

diffusiophoretic coefficients

self-diffusiophoretic force:

$$\mathbf{F}_{\rm sd} = F_{\rm sd}\mathbf{u}$$

particle director $\mathbf{u}$: $\|\mathbf{u}\| = 1$

$$F_{\rm sd} = \frac{4\pi\eta R}{1+3b/R}\left(\frac{b_{\rm B}}{D_{\rm B}} - \frac{b_{\rm A}}{D_{\rm A}}\right)(\kappa_+\bar{c}_{\rm A} - \kappa_-\bar{c}_{\rm B})a_1 = \gamma\,\chi\,W_{\rm rxn}$$

reaction rate

diffusiophoretic coupling

diffusiophoretic velocity: $\mathbf{V}_{\rm sd} = V_{\rm sd}\,\mathbf{u}$ with $V_{\rm sd} = \frac{F_{\rm sd}}{\gamma} = \chi W_{\rm rxn}$ $\qquad \beta D = \frac{D}{k_{\rm B}T} = \frac{1}{\gamma}$

overdamped translational Langevin equation:

$$\frac{d\mathbf{r}}{dt} = V_{\rm sd}\mathbf{u} + \beta D\mathbf{F}_{\rm ext} + \mathbf{V}_{\rm fluct}(t)$$

overdamped rotational Langevin equation:

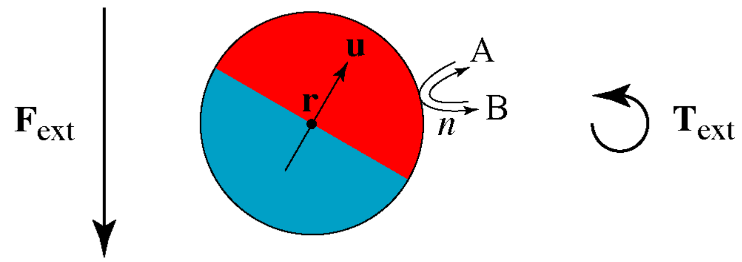
$$\frac{d\mathbf{u}}{dt} = \mathbf{u}\times\left[\beta D_{\rm rot}\mathbf{T}_{\rm ext} + \boldsymbol{\Omega}_{\rm fluct}(t)\right]$$

P. Gaspard & R. Kapral, J. Chem. Phys. **147** (2017) 211101

MECHANOCHEMICAL COUPLING

Janus particle propelled by the self-diffusiophoretic effect of the reaction A↔B

orientation **u**: $\|\mathbf{u}\| = 1$
position $\mathbf{r} = (x,y,z)$
reaction counter n



Onsager reciprocal relation:
symmetric matrix of linear response coefficients between the affinities and the currents:

$$\frac{d\mathbf{r}}{dt} = \beta D \mathbf{F}_{\rm ext} + V_{\rm sd}\mathbf{u} + \mathbf{V}_{\rm fluct}(t)$$

$$\frac{dn}{dt} = \,?\, + W_{\rm rxn} + W_{\rm fluct}(t)$$

self-diffusiophoretic propulsion

$$\frac{d}{dt}\begin{pmatrix}\mathbf{r}\\ n\end{pmatrix} = \begin{pmatrix} D\mathbf{1} & \chi D_{\rm rxn}\mathbf{u} \\ \chi D_{\rm rxn}\mathbf{u} & D_{\rm rxn}\end{pmatrix}\begin{pmatrix}\mathbf{A}_{\rm mech}\\ A_{\rm rxn}\end{pmatrix} + \begin{pmatrix}\mathbf{V}_{\rm fluct}(t)\\ W_{\rm fluct}(t)\end{pmatrix}$$

prediction of microreversibility Gaussian white noises ↑

mechanical affinity: $$\mathbf{A}_{\rm mech} \equiv \beta \mathbf{F}_{\rm ext} = \frac{\mathbf{F}_{\rm ext}}{k_{\rm B}T}$$

chemical affinity in linear regime: $$A_{\rm rxn} = \ln\frac{W_+}{W_-} \approx \frac{W_{\rm rxn}}{D_{\rm rxn}}$$

$$W_{\rm rxn} \equiv W_+ - W_- \qquad W_+ = k_+ \bar{c}_{\rm A}$$

$$D_{\rm rxn} \equiv \frac{1}{2}\left(W_+ + W_-\right) \qquad W_- = k_- \bar{c}_{\rm B}$$

P. Gaspard & R. Kapral, J. Chem. Phys. **147** (2017) 211101

COUPLED LANGEVIN EQUATIONS

Janus particle propelled by the self-diffusiophoretic effect of the reaction A↔B

number n of reactive events; position $\mathbf{r} = (x,y,z)$; orientation $\mathbf{u}$: $\|\mathbf{u}\| = 1$

chemical overdamped Langevin equation:

$$\frac{dn}{dt} = W_{\rm rxn} + \beta \boxed{\chi} D_{\rm rxn} \mathbf{u}\cdot \mathbf{F}_{\rm ext} + W_{\rm fluct}(t)$$

translational overdamped Langevin equation:

$$\frac{d\mathbf{r}}{dt} = \boxed{\chi} W_{\rm rxn} \mathbf{u} + \beta D \mathbf{F}_{\rm ext} + \mathbf{V}_{\rm fluct}(t)$$

rotational overdamped Langevin equation:

$$\frac{d\mathbf{u}}{dt} = \mathbf{u} \times \left[\beta D_{\rm rot} \mathbf{T}_{\rm ext} + \boldsymbol{\Omega}_{\rm fluct}(t) \right]$$

Gaussian white noises:

$$\langle W_{\rm fluct}(t) \rangle = 0$$
$$\langle \mathbf{V}_{\rm fluct}(t) \rangle = 0$$
$$\langle \boldsymbol{\Omega}_{\rm fluct}(t) \rangle = 0$$

$$\langle W_{\rm fluct}(t)\, W_{\rm fluct}(t') \rangle = 2 D_{\rm rxn} \delta(t-t')$$
$$\langle W_{\rm fluct}(t)\, \mathbf{V}_{\rm fluct}(t') \rangle = 2 \chi D_{\rm rxn} \mathbf{u}\, \delta(t-t')$$
$$\langle \mathbf{V}_{\rm fluct}(t) \otimes \mathbf{V}_{\rm fluct}(t') \rangle = 2D\, \mathbf{1}\, \delta(t-t')$$
$$\langle \boldsymbol{\Omega}_{\rm fluct}(t) \otimes \boldsymbol{\Omega}_{\rm fluct}(t') \rangle = 2D_{\rm rot} \mathbf{1}\, \delta(t-t')$$

reaction rate $W_{\rm rxn}$; reaction diffusivity $D_{\rm rxn}$; fluctuating rate $W_{\rm fluct}(t)$

external force $\mathbf{F}_{\rm ext}$; translational diffusivity D ; fluctuating velocity $\mathbf{V}_{\rm fluct}(t)$

external torque $\mathbf{T}_{\rm ext}$; rotational diffusivity $D_{\rm rot}$; fluctuating torque $\mathbf{T}_{\rm fluct}(t)$

self-diffusiophoretic velocity: $V_{\rm sd} = \chi W_{\rm rxn}$ ***χ = diffusiophoretic coupling parameter***

P. Gaspard & R. Kapral, J. Chem. Phys. **147** (2017) 211101

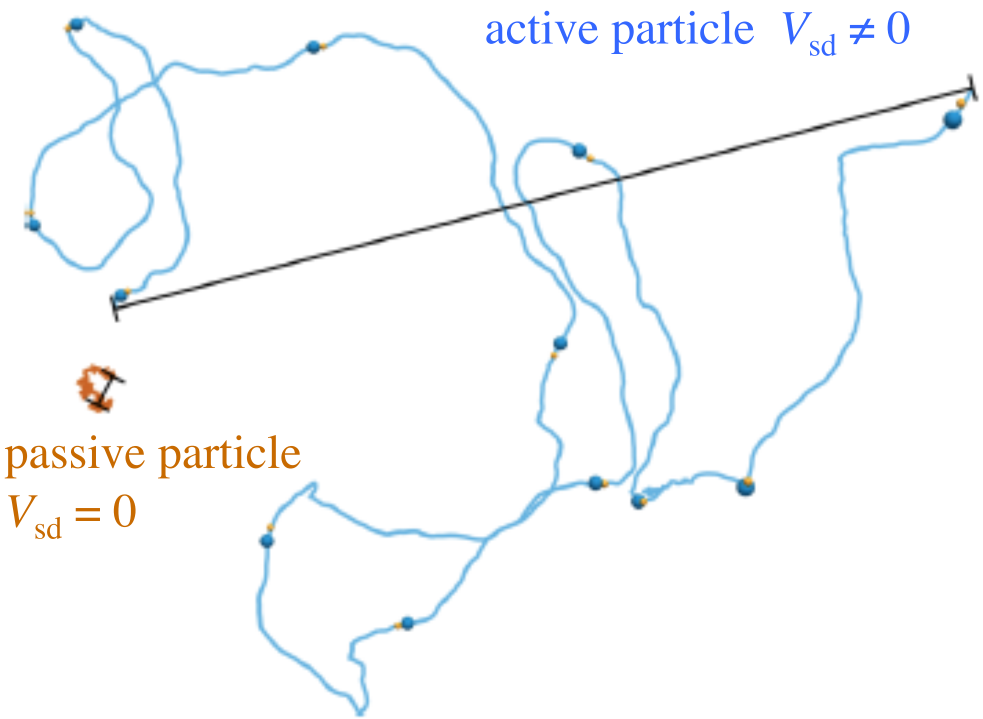
ENHANCED DIFFUSION OF ACTIVE PARTICLES

$\mathbf{F}_{\mathrm{ext}} = 0,\ \mathbf{B}_{\mathrm{ext}} = 0$

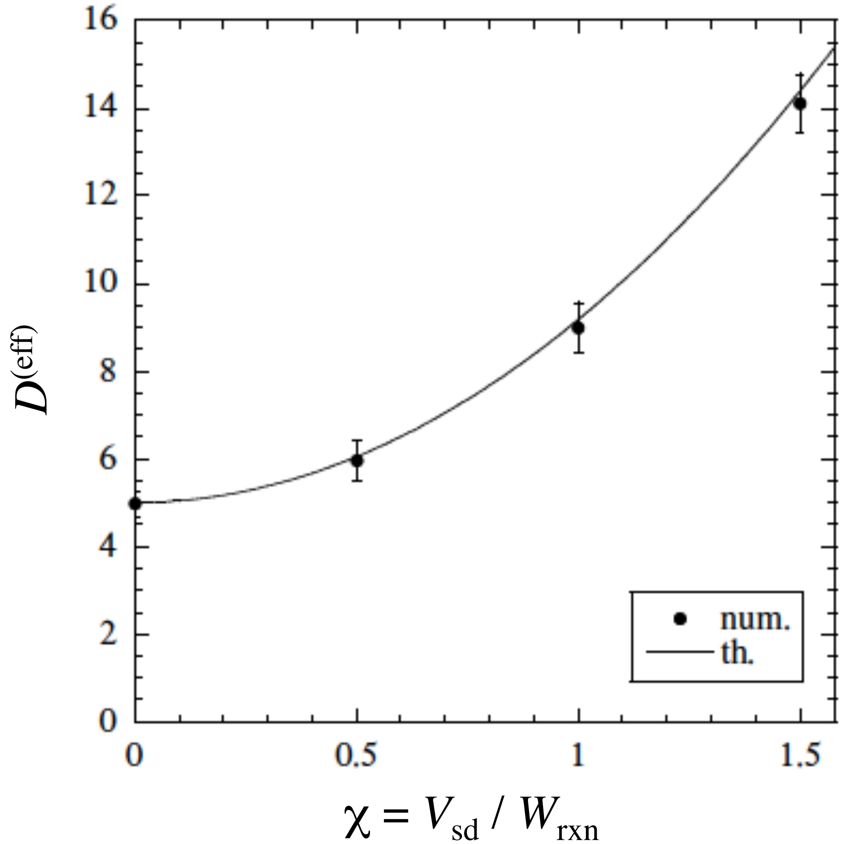
diffusion enhancement due to self-diffusiophoretic velocity V_{sd} :

$$D_t^{(\mathrm{eff})} = D_t + \frac{V_{\mathrm{sd}}^2}{6D_r}$$

self-diffusiophoretic velocity: $V_{\mathrm{sd}} = \chi W_{\mathrm{rxn}}$



$k_B T = 1,\ D_r = 1,\ D = 5,\ W_{\mathrm{rxn}} = 5,\ D_{\mathrm{rxn}} = 2$

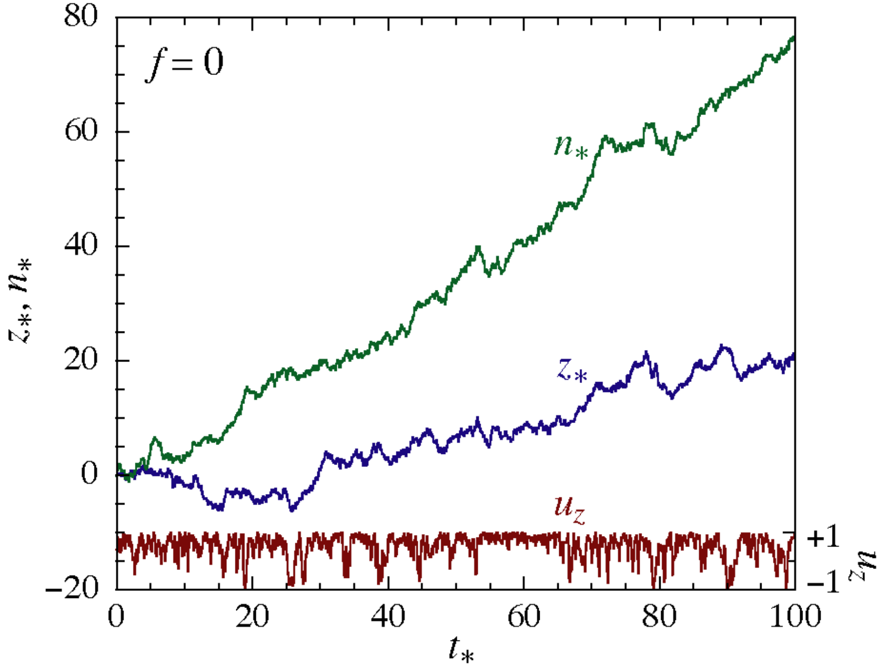


P. H. Colberg, S. Yik Reigh, B. Robertson & R. Kapral, Acc. Chem. Res. **47** (2014) 3504

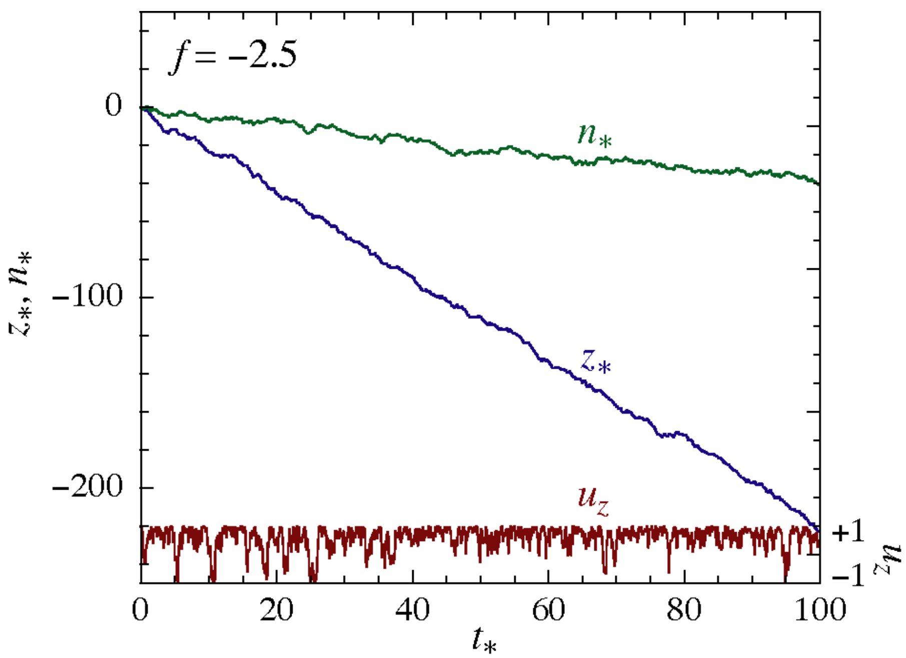
INTEGRATION OF COUPLED STOCHASTIC EQUATIONS

Janus particle propelled by the self-diffusiophoretic effect of the reaction A↔B with an external force and magnetic field in the *z*-direction

domain I: mechanical work



domain II: fuel synthesis



rescaled external force	$f \equiv \beta F \sqrt{D/D_{\text{rot}}}$	$W_{\text{rxn}}/\sqrt{D_{\text{rxn}} D_{\text{rot}}} = 0.8$
rescaled time	$t_* \equiv D_{\text{rot}} t$	$\chi \sqrt{D_{\text{rxn}}/D} = 0.8$
rescaled position in *z*-direction	$z_* \equiv z\sqrt{D_{\text{rot}}/D}$	$\beta \mu B = 2$
rescaled number of reactive events	$n_* \equiv n\sqrt{D_{\text{rot}}/D_{\text{rxn}}}$	$\mathbf{F}_{\text{ext}} = (0,0,F)$
oriention in *z*-direction	u_z	$\mathbf{T}_{\text{ext}} = \mu \mathbf{u} \times \mathbf{B}_{\text{ext}}$
		$\mathbf{B}_{\text{ext}} = (0,0,B)$

P. Gaspard & R. Kapral, J. Chem. Phys. **147** (2017) 211101

MECHANOCHEMICAL COUPLING

The chemical reaction depends on the external force

$$\frac{d\langle \mathbf{X} \rangle}{dt} = \mathbf{L} \cdot \mathbf{A} \quad \begin{cases} \text{mean velocity:} & \dfrac{d\langle \mathbf{r} \rangle}{dt} = V_{\text{sd}} \langle \mathbf{u} \rangle + \beta D \mathbf{F}_{\text{ext}} \\ \text{mean reaction rate:} & \dfrac{d\langle n \rangle}{dt} = W_{\text{rxn}} + \beta \chi D_{\text{rxn}} \langle \mathbf{u} \rangle \cdot \mathbf{F}_{\text{ext}} \end{cases}$$

stall force: $F_{\text{stall}} = -V_{\text{sd}} \langle u_z \rangle / (\beta D)$

synthesis: $F < F_0 = -W_{\text{rxn}} / (\beta \chi D_{\text{rxn}} \langle u_z \rangle)$

rescaled quantities:

$$f \equiv \beta F \sqrt{D/D_{\text{rot}}}$$

$$\dot{\mathbf{r}}_* \equiv \dot{\mathbf{r}} / \sqrt{D D_{\text{rot}}}$$

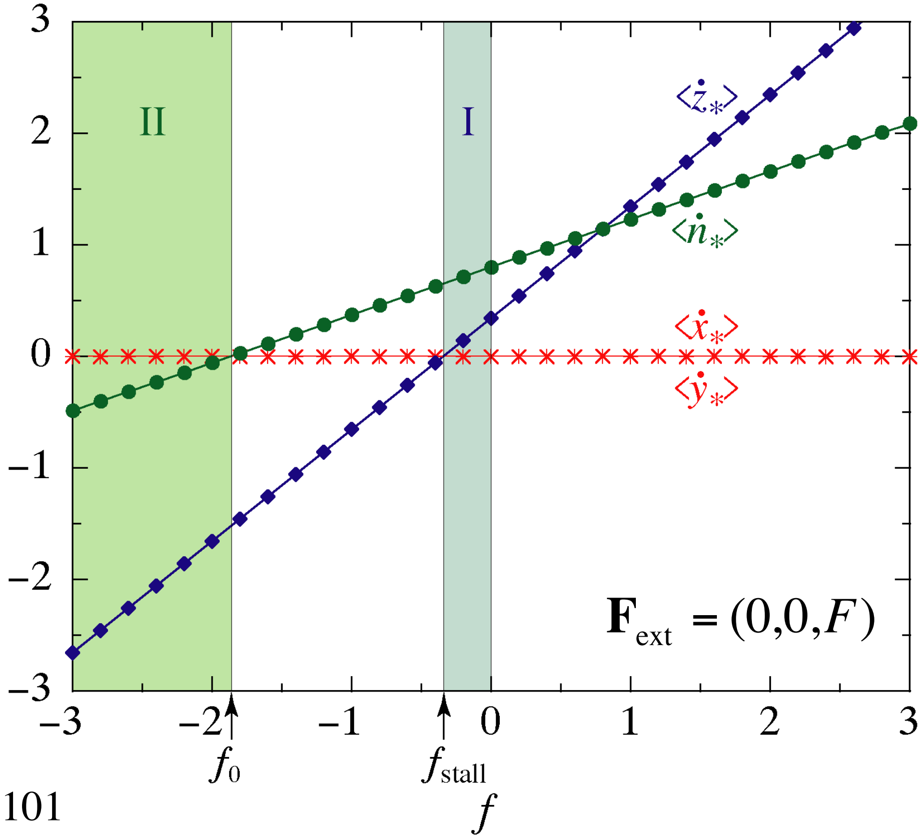
$$\dot{n}_* \equiv \dot{n} / \sqrt{D_{\text{rxn}} D_{\text{rot}}}$$

parameters:

$$W_{\text{rxn}} / \sqrt{D_{\text{rxn}} D_{\text{rot}}} = 0.8$$

$$\chi \sqrt{D_{\text{rxn}} / D} = 0.8$$

$$\beta \mu B = 2$$

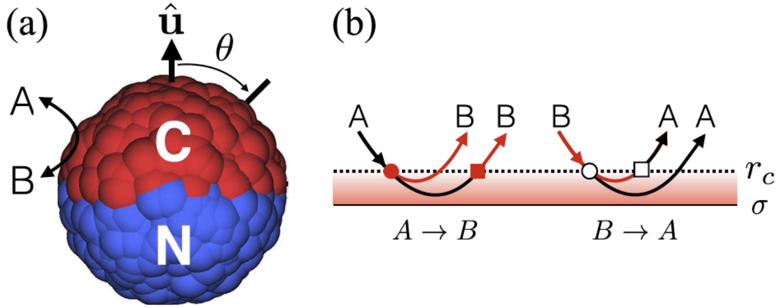


P. Gaspard & R. Kapral, J. Chem. Phys. **147** (2017) 211101

MICROSCOPICALLY REVERSIBLE SIMULATION

System: Janus particle composed of 2681 beads interacting by harmonic potentials
+ 1244220 inert solvent particles + 1244219 reactive particles A and B.

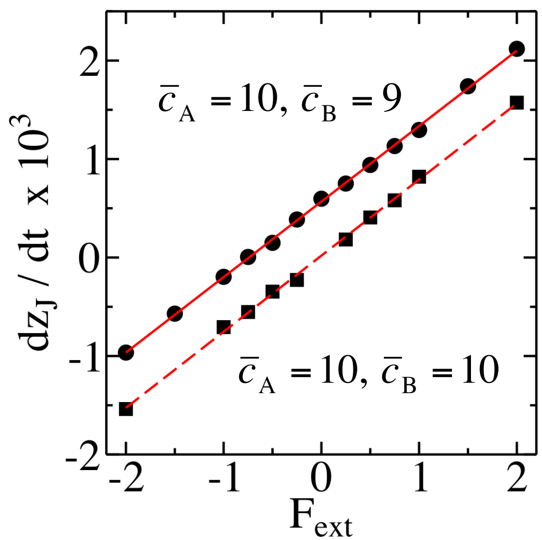
Dynamics: Lennard-Jones interactions of the solution particles with the beads
+ multiparticle collision method among the solution particles
+ stochastic reaction A↔B satisfying detailed balance at equilibrium.

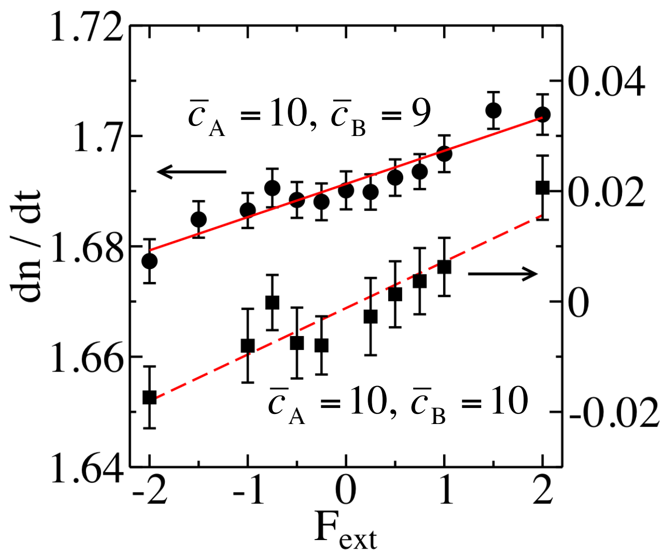


$\frac{\partial\langle\dot{n}\rangle}{\partial F_{ext}}$	$\bar{c}_A = 10,\ \bar{c}_B = 9$	$\bar{c}_A = 10,\ \bar{c}_B = 10$
th.	0.006	0.0063
num.	0.006 ± 0.0006	0.0084 ± 0.0012

$\kappa_+ = \kappa_-$ $\mu B = 500$

V_{sd}	$\bar{c}_A = 10,\ \bar{c}_B = 9$	$\bar{c}_A = 10,\ \bar{c}_B = 10$
th.	6.2×10^{-4}	0
num.	6.0×10^{-4}	1.0×10^{-5}



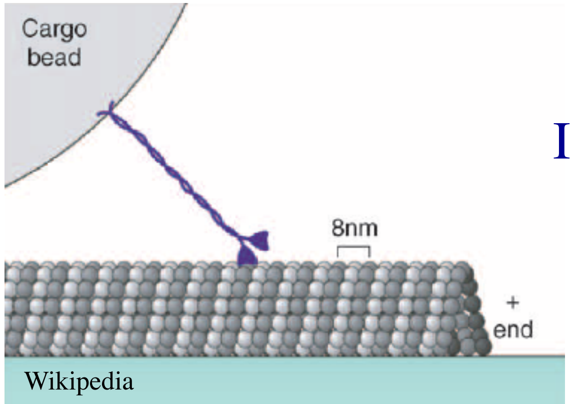


M.-J. Huang, J. Schofield, P. Gaspard & R. Kapral, J. Chem. Phys. **149** (2018) 024904

MECHANOCHEMICAL COUPLING FOR ENERGY TRANSDUCTION

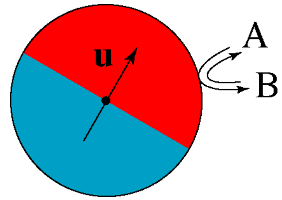
MOLECULAR MOTORS

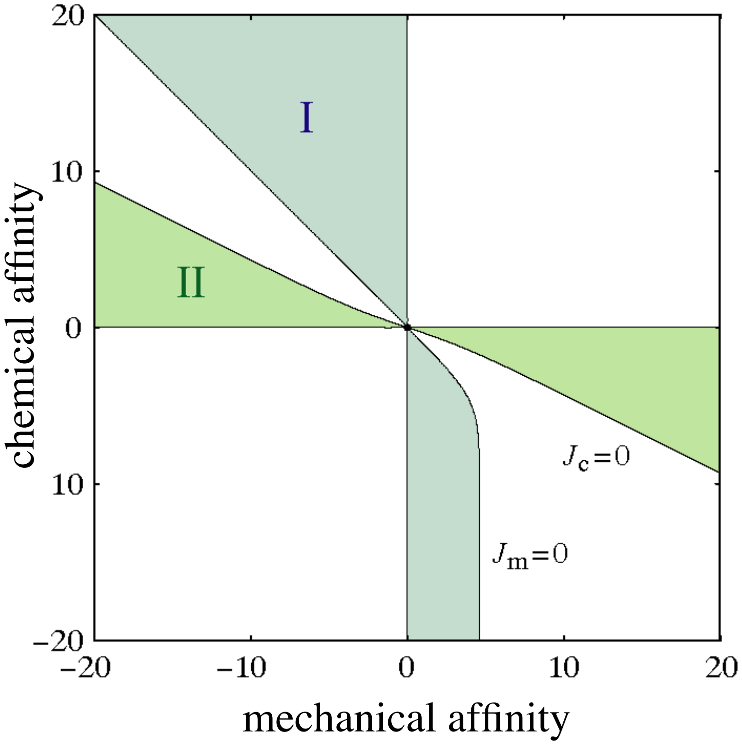
ACTIVE PARTICLES

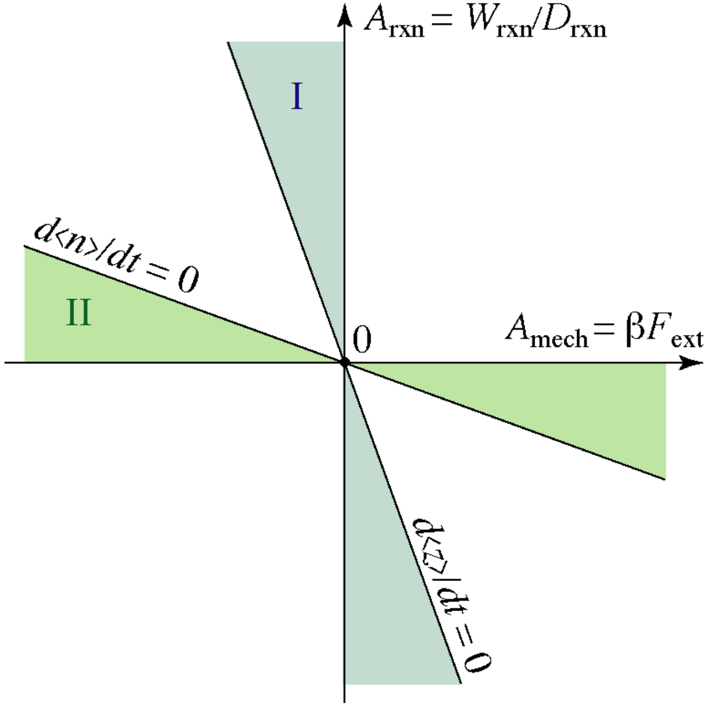


I: mechanical work

II: fuel synthesis







F. Jülicher, A. Ajdari & J. Prost, Rev. Mod. Phys. **69** (1997) 1269 P. Gaspard & R. Kapral, J. Chem. Phys. **148** (2018) 134104

MECHANOCHEMICAL FLUCTUATION THEOREM

for the coupled Langevin equations

$$\frac{P(\mathbf{r},n,t)}{P(-\mathbf{r},-n,t)} \approx_{t\to\infty} \exp\left(\mathbf{A}_{\rm mech}\cdot\mathbf{r} + A_{\rm rxn} n\right)$$

$$\Rightarrow \frac{1}{k_{\rm B}}\frac{d_{\rm i}S}{dt} = \mathbf{A}_{\rm mech}\cdot\langle\dot{\mathbf{r}}\rangle + A_{\rm rxn}\langle\dot{n}\rangle \geq 0$$

Numerical integration of the coupled Langevin equations

rescaled quantities: $z_* \equiv z\sqrt{D_{\rm rot}/D}$

$n_* \equiv n\sqrt{D_{\rm rot}/D_{\rm rxn}}$

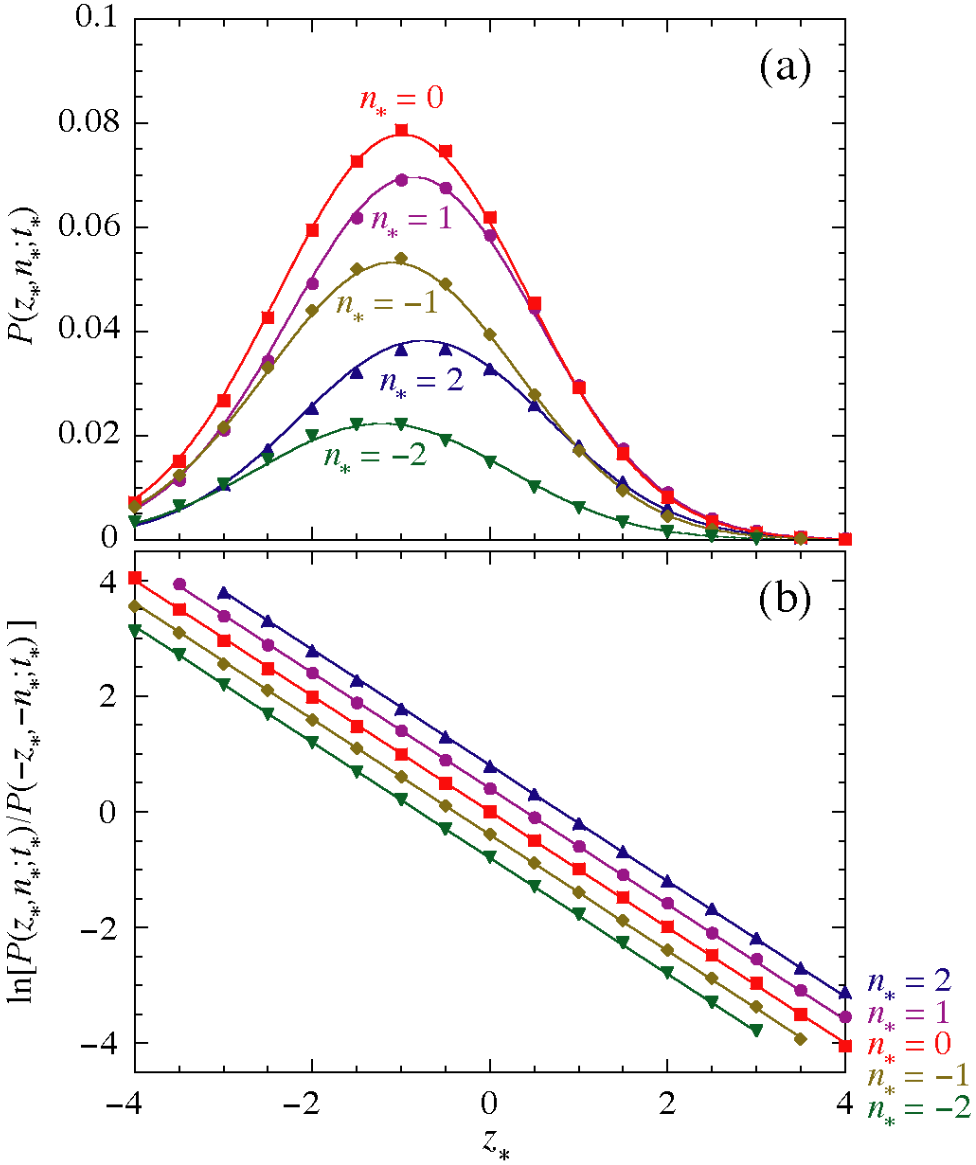
$t_* \equiv D_{\rm rot} t = 1$

parameters: $f \equiv \beta F \sqrt{D/D_{\rm rot}} = -1$

$W_{\rm rxn}/\sqrt{D_{\rm rxn}D_{\rm rot}} = 0.4$

$\chi\sqrt{D_{\rm rxn}/D} = 0.4$

$\beta\mu B = 1$



P. Gaspard & R. Kapral, J. Chem. Phys. **147** (2017) 211101

FLUCTUATION THEOREM & EFFECTIVE TEMPERATURE

mechanochemical fluctuation theorem:

$$\frac{P(\mathbf{r},n,t)}{P(-\mathbf{r},-n,t)} \approx_{t\to\infty} \exp\left(\frac{\mathbf{F}_{\text{ext}}\cdot\mathbf{r}}{k_{\text{B}}T} + A_{\text{rxn}}n\right)$$

Gaussian distribution on long-time scales:
effective mechanical fluctuation theorem for the marginal distribution $p(z,t)$:

$$\frac{p(z,t)}{p(-z,t)} \approx_{t\to\infty} \exp\left(\frac{F^{(\text{eff})}z}{k_{\text{B}}T^{(\text{eff})}}\right)$$

effective force:

$$F^{(\text{eff})} = F_{\text{ext}} + \gamma V_{\text{sd}}\langle u_z\rangle \qquad (\mathbf{B}_{\text{ext}} \neq 0)$$

Justification for the introduction
of an effective temperature
for the biased random walk of
active particles driven
away from equilibrium.

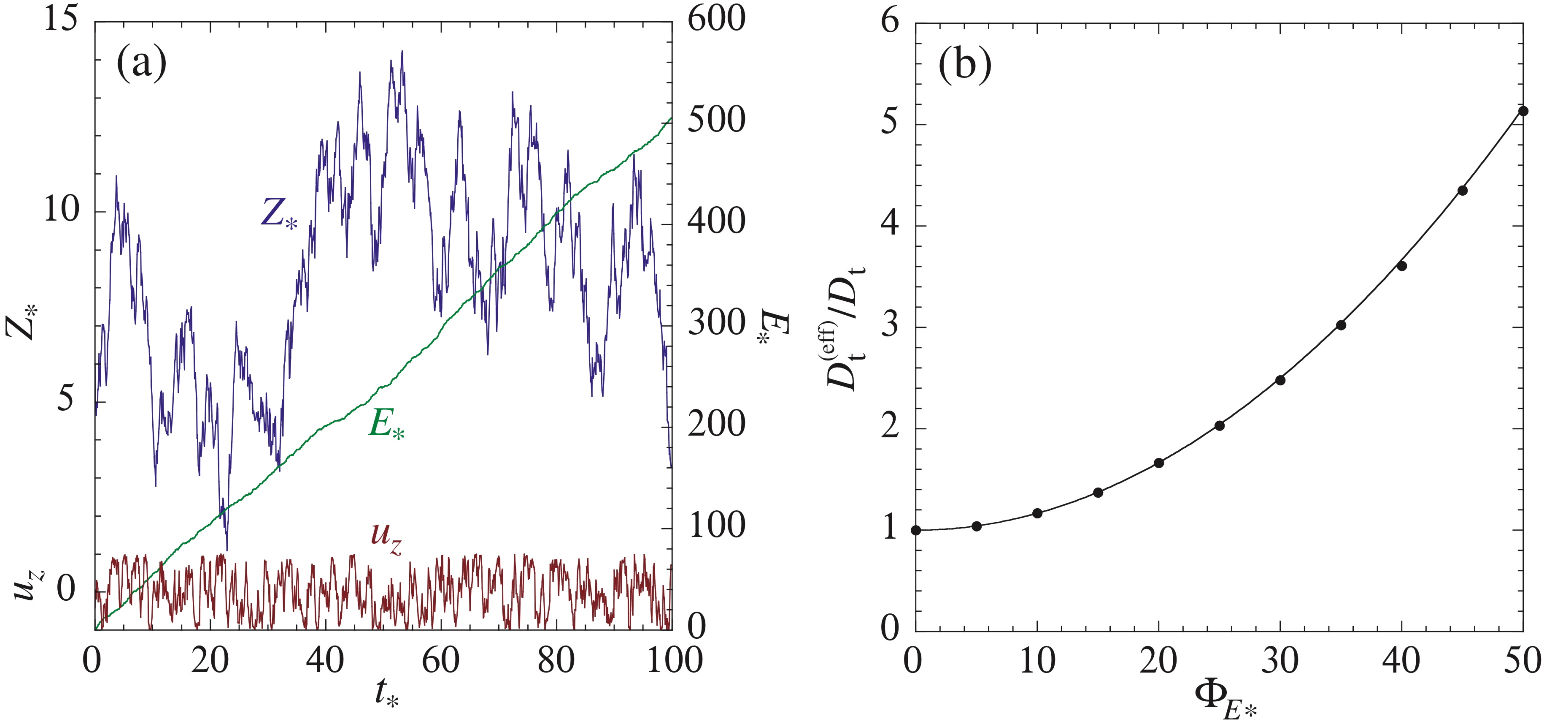
$$T^{(\text{eff})} = T\frac{D_{\text{t}}^{(\text{eff})}}{D_{\text{t}}} = T\left(1 + \frac{V_{\text{sd}}^2}{6D_{\text{r}}D_{\text{t}}}\right)$$

This effective temperature is
larger than the actual temperature.

P. Gaspard & R. Kapral, J. Chem. Phys. **147** (2017) 211101

JANUS PARTICLES PROPELLED BY SELF-THERMOPHORESIS

Janus particle propelled by the self-thermophoretic effect
of hemispheric radiative heating at the net rate $\Phi_{E*} = \Phi_E / \sqrt{D_E D_r}$



rescaled time $t_* \equiv D_r t$

rescaled position in z-direction $Z_* \equiv Z\sqrt{D_r / D_t}$

rescaled transferred radiative energy $E_* \equiv E\sqrt{D_r / D_E}$

$\Phi_{E*} = \Phi_E / \sqrt{D_E D_r} = 5 \qquad \chi\sqrt{D_E / D_t} = 0.1$

$$D_t^{(eff)} = D_t + \frac{\chi^2 \Phi_E^2}{6 D_r}$$

diffusion enhancement
by propulsion combined
with random rotation

P. Gaspard & R. Kapral, J. Stat. Mech. (2019) 074001

2. COLLECTIVE DYNAMICS OF MANY ACTIVE PARTICLES

SYSTEMS WITH MANY ACTIVE PARTICLES

N motors with positions $\mathbf{r}_i$ and orientations $\mathbf{u}_i$ interacting via the molecular concentrations and their gradients $\mathbf{g}_k$: diffusiophoretic linear and angular velocities

$$\mathbf{V}_{\mathrm{d}} = \frac{\mathbf{F}_{\mathrm{d}}}{\gamma_{\mathrm{t}}} = V_{\mathrm{sd}}\mathbf{u} + \sum_k \left[\xi_k \mathbf{1} + \varepsilon_k \left(\mathbf{uu} - \frac{1}{3}\mathbf{1} \right) \right] \cdot \mathbf{g}_k \qquad \Omega_{\mathrm{d}} = \frac{\mathbf{T}_{\mathrm{d}}}{\gamma_{\mathrm{r}}} = \sum_k \lambda_k \mathbf{u} \times \mathbf{g}_k$$

$$V_{\mathrm{sd}} = \chi\Gamma\left(\kappa_+^{\mathrm{c}}\bar{c}_{\mathrm{A}} - \kappa_-^{\mathrm{c}}\bar{c}_{\mathrm{B}}\right) \qquad W_{\mathrm{rxn}} = \Gamma\left(\kappa_+^{\mathrm{c}}\bar{c}_{\mathrm{A}} - \kappa_-^{\mathrm{c}}\bar{c}_{\mathrm{B}}\right)$$

Distribution function of the colloidal motors:

$$f(\mathbf{r},\mathbf{u},t) = \sum_{i=1}^{N} \delta^3\left[\mathbf{r} - \mathbf{r}_i(t)\right] \, \delta^2\left[\mathbf{u} - \mathbf{u}_i(t)\right]$$

Evolution equations of the distribution function and molecular concentrations:

$$\partial_t f + \nabla\cdot\left(\mathbf{V}f - D_{\mathrm{t}}\nabla f\right) = D_{\mathrm{r}}\hat{L}_{\mathrm{r}} f \qquad \hat{L}_{\mathrm{r}} f = \frac{1}{\sin\theta}\partial_\theta\left[\sin\theta e^{-\beta U_{\mathrm{t}}}\partial_\theta\left(\mathrm{e}^{\beta U_{\mathrm{t}}} f\right)\right] + \frac{1}{\sin^2\theta}\partial_\varphi\left[e^{-\beta U_{\mathrm{t}}}\partial_\varphi\left(\mathrm{e}^{\beta U_{\mathrm{t}}} f\right)\right]$$

$$\partial_t n_k + \nabla\cdot \mathbf{j}_k = \nu_k w \qquad (k = \mathrm{A,B})$$

Onsager's principle of linear regression can be used to determine the fluxes in terms of the affinities including the external force and torque:

$$\left\langle J_\alpha \right\rangle = \sum_\beta L_{\alpha\beta} A_\beta \qquad \frac{1}{k_{\mathrm{B}}}\frac{d_{\mathrm{i}}S}{dt} = \sum_\alpha A_\alpha \left\langle J_\alpha \right\rangle = \sum_\alpha L_{\alpha\beta} A_\alpha A_\beta \geq 0$$

P. Gaspard & R. Kapral, Research (2020) 973923; arXiv:2003.06861

CLUSTERING OF ACTIVE PARTICLES: THEORY

System: • colloidal motors at the concentration c
• reaction A↔B at the motor surfaces and in the bulk

Special diffusion-reaction equations with chemotactic velocity as ∇a for the motor concentration c, coupled to the fuel concentration a (the product concentration being $b = n_0 - a$)

$$\partial_t c = \nabla \cdot \left[\left(D_\mathrm{t} + \tau_\mathrm{r} V_\mathrm{sd}^2 \right) \nabla c - \left(\xi + \sigma V_\mathrm{sd} \right) c \nabla a \right]$$

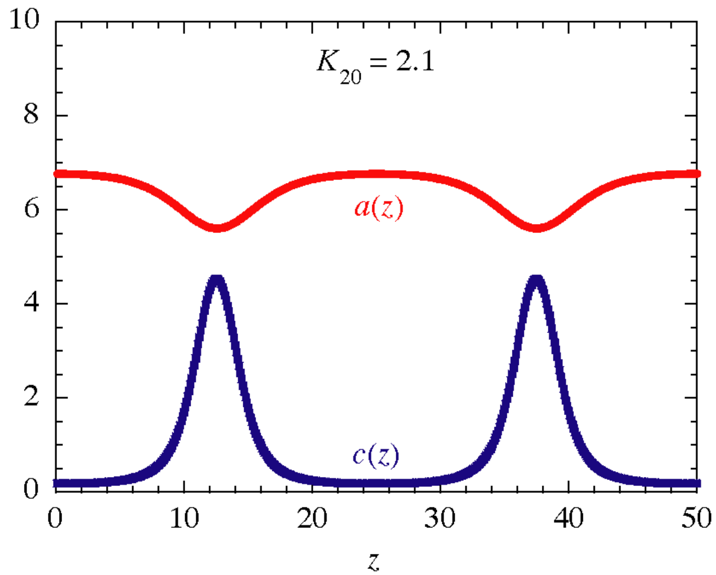
$$V_\mathrm{sd} = V_0 + \zeta a$$

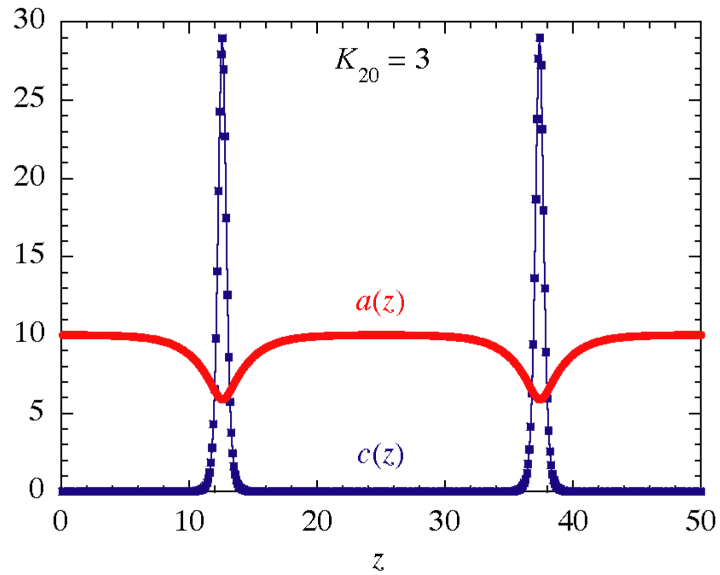
$$\partial_t a = D \nabla^2 a - W_\mathrm{tot}$$

$$W_\mathrm{tot} = c\left(Ka - K_0 \right) + K_2 a - K_{20}$$

clustering instability from uniform state (a_0, c_0) if

$$c_0 \left(\xi + \sigma V_\mathrm{sd} \right)\left(Ka_0 - K_0 \right) + \left(Kc_0 + K_2 \right)\left(D_\mathrm{t} + \tau_\mathrm{r} V_\mathrm{sd}^2 \right) < 0$$





$c_0 = 1,\ n_0 = 10,\ D = D_\mathrm{t} = \tau_\mathrm{r} = 1,\ \xi = -3,\ \sigma = -2,\ \zeta = 0.1,\ V_0 = 0.2,\ K = 0.2,\ K_0 = 1,\ K_2 = 0.3$ threshold: $K_{20} \approx 1.943$

CLUSTERING OF ACTIVE PARTICLES: THEORY

Stability analysis using the density or the distribution function of colloidal motors

with the density:

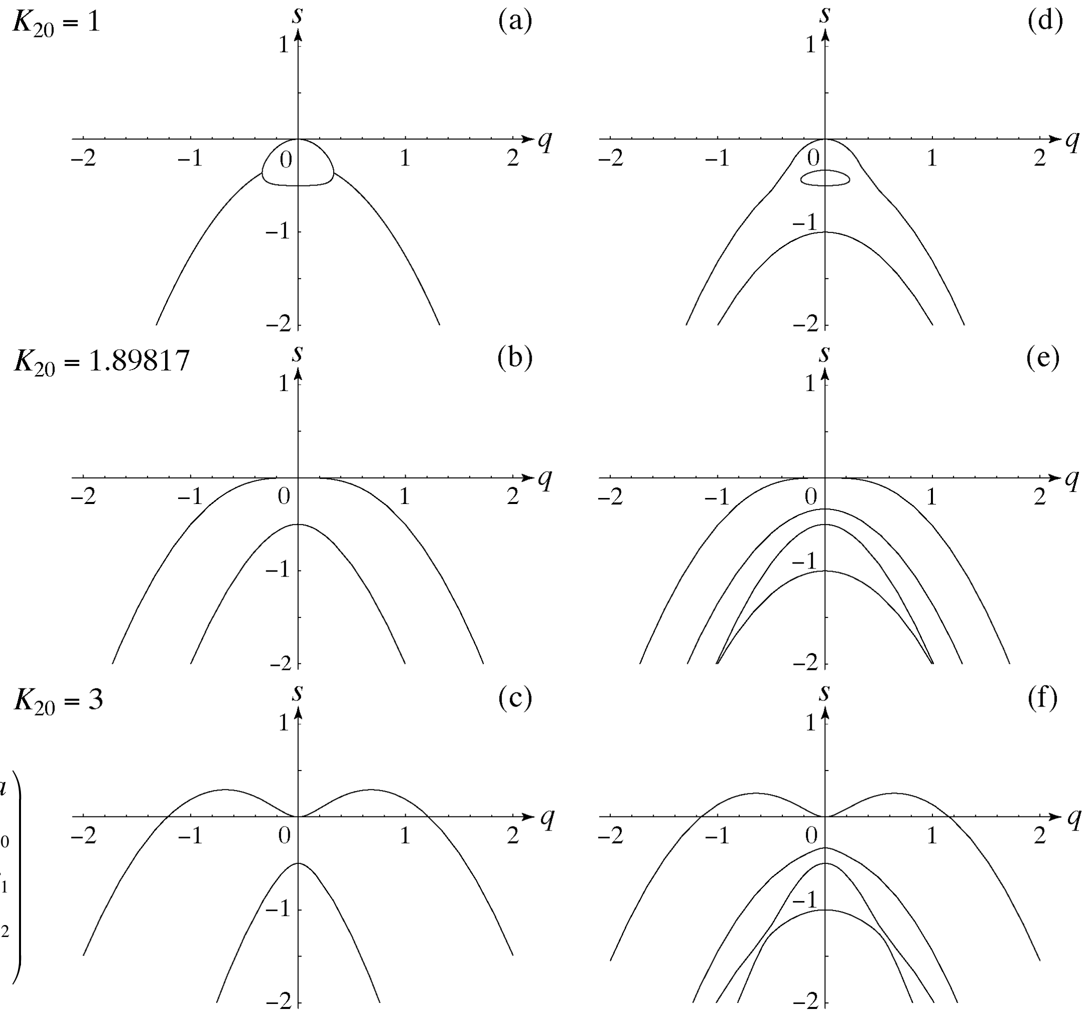
$$\partial_t \begin{pmatrix} \delta a \\ \delta c \end{pmatrix} = \begin{pmatrix} -Dq^2 - \tilde{K} & -w \\ \rho q^2 & -D_{\rm t}^{\rm (eff)} q^2 \end{pmatrix} \begin{pmatrix} \delta a \\ \delta c \end{pmatrix}$$

$$D_{\rm t}^{\rm (eff)} = D_{\rm t} + \frac{V_{\rm sd}^2}{6D_{\rm r}}$$

with the distribution function:

$$\delta f = \frac{1}{4\pi} \sum_{l=0}^{\infty} \delta c_l P_l(\cos\theta)$$

$$\partial_t \begin{pmatrix} \delta a \\ \delta c_0 \\ \delta c_1 \\ \delta c_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} -Dq^2 - \tilde{K} & -w & 0 & 0 & \cdots \\ c_0 \xi q^2 & -D_{\rm t} q^2 & -iV_{\rm sd} q/3 & 0 & \cdots \\ ic_0(2\lambda - \zeta)q & -iV_{\rm sd} q & -D_{\rm t} q^2 - 2D_{\rm r} & -i2V_{\rm sd} q/5 & \cdots \\ c_0 2\varepsilon q^2/3 & 0 & -i2V_{\rm sd} q/3 & -D_{\rm t} q^2 - 6D_{\rm r} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \delta a \\ \delta c_0 \\ \delta c_1 \\ \delta c_2 \\ \vdots \end{pmatrix}$$



$c_0 = 1,\ n_0 = 10,\ D = D_{\rm t} = \tau_{\rm r} = 1,\ \xi = -3,\ \sigma = -2,\ \zeta = 0.1,\ V_0 = 0.5,\ K = 0.2,\ K_0 = 1,\ K_2 = 0.3$ threshold: $K_{20} \approx 1.89817$

P. Gaspard & R. Kapral, Research (2020) 973923; arXiv:2003.06861

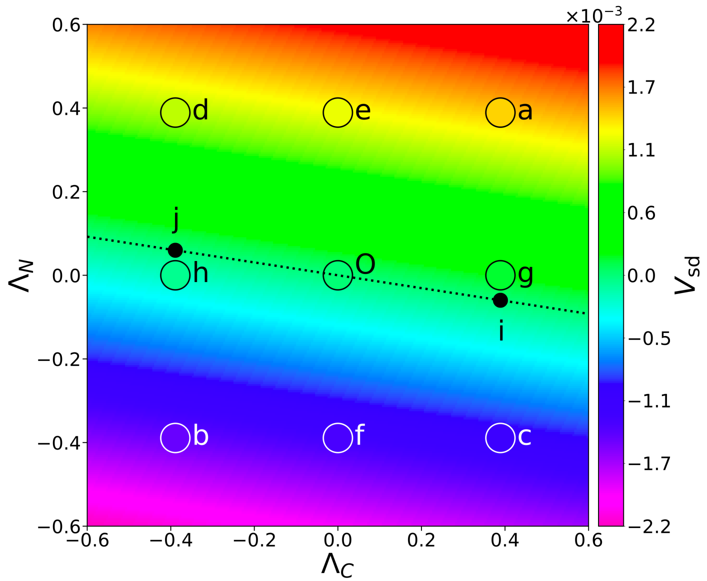
CLUSTERING OF ACTIVE PARTICLES: SIMULATIONS

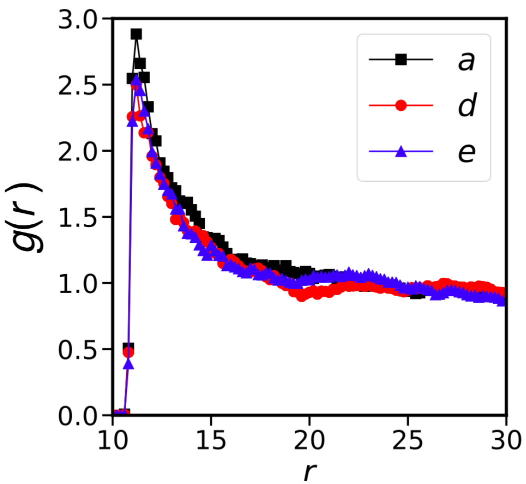
System: 20 Janus motors with different diffusiophoresis on both hemispheres
+ inert solvent particles + reactive particles A and B.

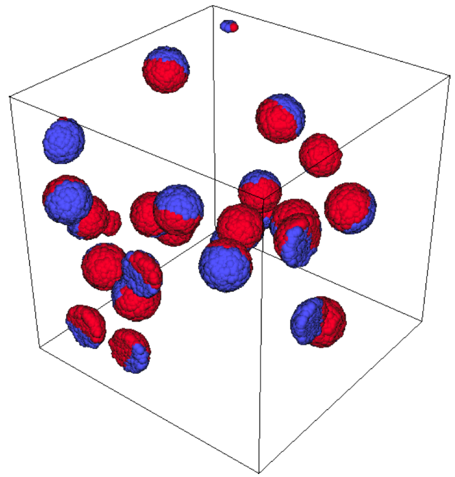
Dynamics: molecular dynamics + multiparticle collision method for the solution
+ stochastic reaction A↔B at the motor surfaces and in the bulk.

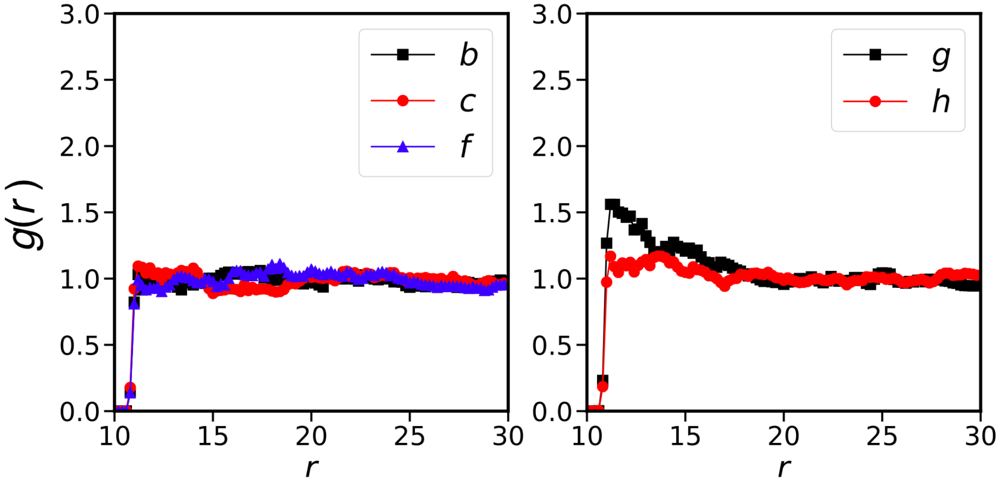
$$V_{\rm sd} = -\frac{k_{\rm B}T}{\eta D}\,\frac{\kappa_+ c_{\rm A} - \kappa_- c_{\rm B}}{2(1+2b/R)}\left(\alpha_C\Lambda_C + \alpha_N\Lambda_N\right)$$

$$\Lambda_h = \int_0^{\delta} dz\,(z+b)\left[{\rm e}^{-\beta u_{\rm B}^h(z)} - {\rm e}^{-\beta u_{\rm A}^h(z)}\right]$$









M.-J. Huang, J. Schofield, P. Gaspard & R. Kapral, J. Chem. Phys. **150** (2019) 124110

MOTILITY-INDUCED PHASE SEPARATION

M. E. Cates & J. Tailleur, Annu. Rev. Condens. Matter Phys. **6** (2015) 219
T. Speck, J. Bialké, M. Menzel & H. Löwen, Phys. Rev. Lett. **112** (2014) 218304.

The effective diffusion coefficient may become negative in ***dense*** active suspensions, leading to possible phase separation.

The speed v_0 of active particles decreases with the particle density ρ because of crowding:

$$v(\rho) = v_0(1 - \alpha\rho)$$

$$\tilde{D}_{\mathrm{t}}^{(\mathrm{eff})}(\rho) = D_{\mathrm{t}} + \frac{v_0^2}{6D_{\mathrm{r}}}(1 - \alpha\rho)(1 - 2\alpha\rho)$$

Description with effective Cahn-Hilliard equation: $\partial_t \phi = \nabla^2\left(\phi^3 - \phi - \nabla^2\phi\right)$

Spinodal decomposition: Ostwald ripening: $L(t) \propto t^{1/3}$

CONCLUSION & PERSPECTIVES

- Energy transduction in biomolecular and self-phoretic motors: coupling between chemical reaction and mechanical motion (2 currents)

- Stochastic approach based on fluctuating chemohydrodynamics and interfacial nonequilibrium thermodynamics for the motion of a Janus particle propelled by the self-diffusiophoretic effect of some reaction A↔B.

- Coupled overdamped Langevin equations for the translation, rotation, and reaction of the Janus particle.

- Mechanochemical coupling fixed by microreversibility: Onsager's reciprocal relations & mechanochemical fluctuation theorem.

- Extension to Janus particles propelled by self-thermophoresis.

- Collective dynamics:
  - deduction of mean-field equations & clustering instability in dilute systems
  - towards denser systems: interactions between the active particles

P. Gaspard & R. Kapral, Adv. Phys. X **4** (2019) 1602480
P. Gaspard & R. Kapral, Research (2020) 973923; arXiv:2003.06861