Nanomotors - a review with molecular simulations

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ICTP/SISSA Statistical Physics Seminar - 19 june 2018

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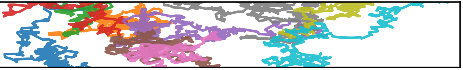


Introduction: what are nanomotors and why are they interesting?

Sedimentation

Chemotaxis

Anisotropic nanomotors

Symmetry breaking

Perspectives

Collaborations

Sedimentation

- Tina Mitteramskogler (KU Leuven)

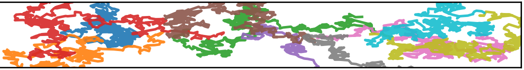
Chemotaxis

- Laurens Deprez (KU Leuven)

Self-propulsion by symmetry-breaking

- Raymond Kapral (University of Toronto)
- Alexander Mikhailov (Fritz-Haber-Institut, Berlin)

Introduction



I will probably forget

- The slides are downloadable `http://pdebuyl.be/`
- You can click on the references to go the bibliography.
- There, you can click on the doi to go to the article.
- The simulations can be reproduced with the open-source codes RMPCDMD and nano-dimer.

Introduction

What are nanomotors?

- 9mm disks Ismagilov *et al* (2002)
- Bimetalic nanorods Paxton *et al* (2004)
- Howse *et al* (2007)
- Ke *et al* (2010)
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- 30 ηm size motor Lee *et al* (2014)
- Sub-ηm motor Pavlick *et al* (2013)

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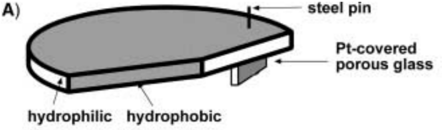

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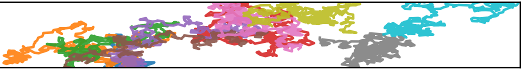

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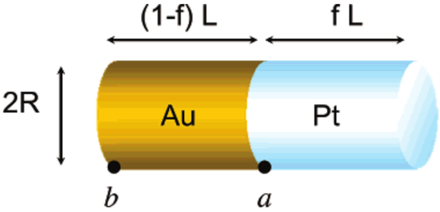

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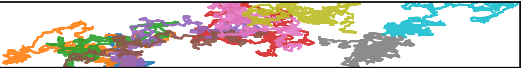

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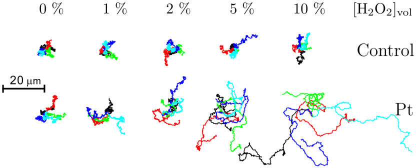
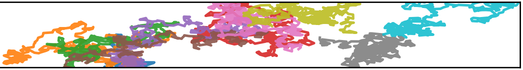


FIG. 1 (color online). Trajectories over 25 sec for ×5 particles of the control (blank) and platinum-coated particles in water and varying solutions of hydrogen peroxide.

Introduction



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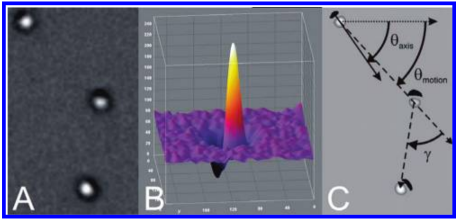

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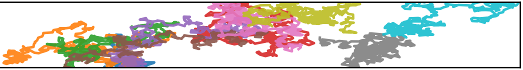

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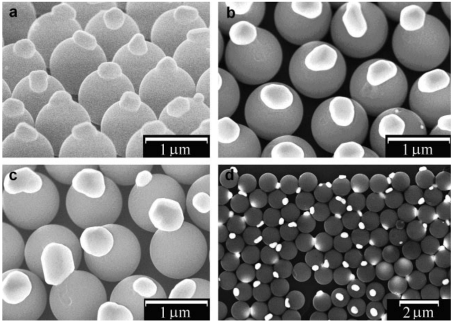
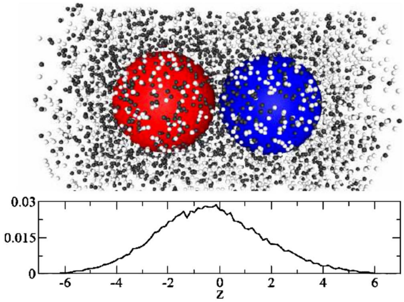


Introduction

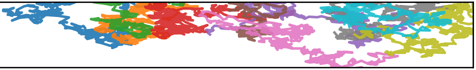
Simulations of nanomotors

- Molecular Dynamics
- The solvent is coarse-grained using "Multiparticle Collision Dynamics".
    - Thermal fluctuations
    - Hydrodynamics
    - Conservation of energy and momentum
- Chemical kinetics



From Rückner and Kapral (2007)

Introduction



How do nanomotors move? - Phoretic theory

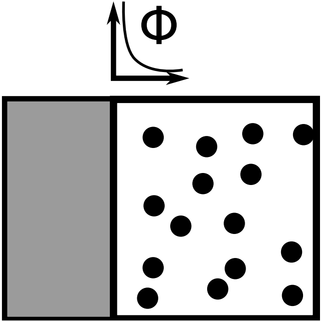
- Stokes equation in the boundary layer returns the slip velocity

$$v^s(\vec{r}) = -\frac{k_B T}{\eta}\Lambda\nabla c(\vec{r})$$

$$\Lambda = \int_0^\infty r[e^{-\Phi(r)/k_B T} - 1]dr$$

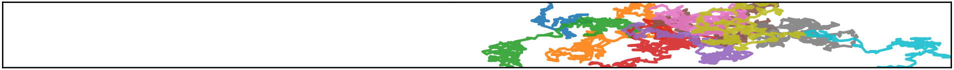
- Potential

$$V(r) = \epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \frac{1}{4}\right)$$



References

- Anderson (1989); Brady (2011); Kapral (2013)



Sedimentation

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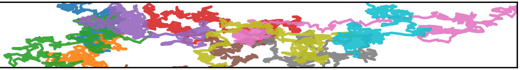
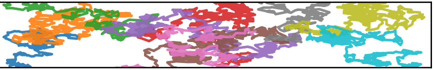


History

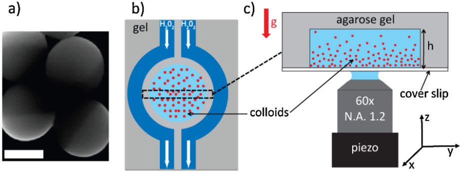
- Key to Einstein's 1905 paper
- Foundational experiment for the atomic theory of matter (Perrin)

Sedimentation



Sedimentation for nanomotors - experiments

- Experiments done by Palacci *et al* (2010)
- First interpretation with an “effective temperature”



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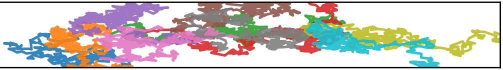
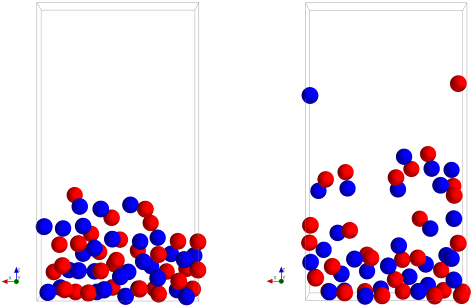


Sedimentation for nanomotors - simulations

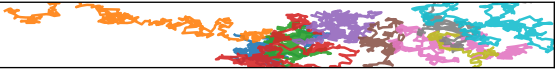
- Dimer nanomotors
- Gravity field



(a) Inactive.

(b) $\epsilon_{\mathrm{NB}} = 0.5$.

Sedimentation



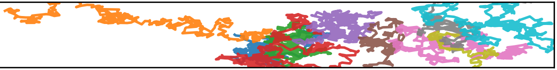
Smoluchowski equation

- System not in equilibrium → no canonical distribution
- Dynamical model, assuming loss of orientational correlation

$$\partial_t c(z) = D_{eff} \partial_z^2 c(z) - mg\mu \partial_z c(z)$$

- $D_{eff} = D + \frac{1}{3} v_{sp}^2 \tau_r$
- Self-propelled velocity v_{sp}
- Rotational time τ_r

Sedimentation



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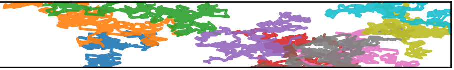
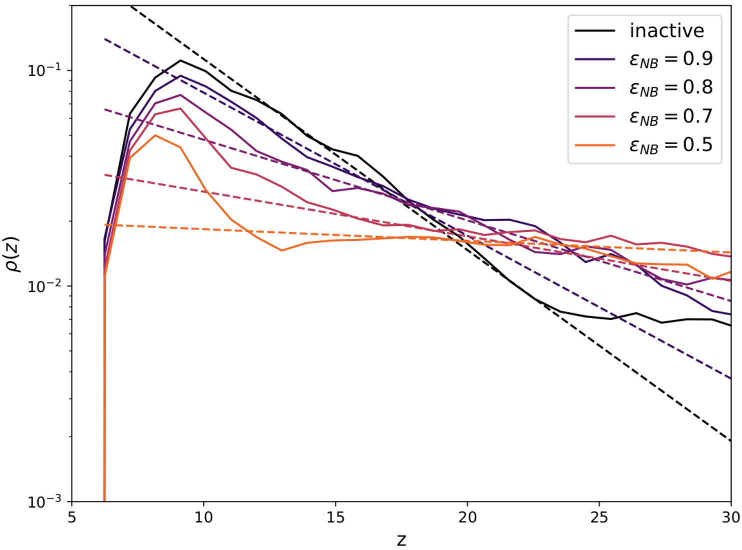
- $D_{eff} = D + \frac{1}{3}v_{sp}^2\tau_r$
- Self-propelled velocity v_{sp}
- Rotational time τ_r
- Sedimentation length:

$$\delta = \frac{k_B T}{mg}\left(1 + \frac{1}{3}\frac{v_{sp}^2\tau_r}{D}\right)$$

Sedimentation





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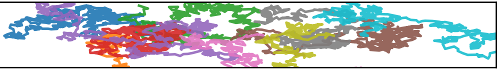

Active sedimentation

- Dynamical model based on the Smoluchowski equation
- Differs from equilibrium by the *active* diffusion
- The simulations also show excess close to the wall, a generic feature of active motion.

Chemotaxis

Chemotaxis

Chromatium okenii

- Miyoshi (1898) J. Coll. Sci. Imp. Univ. Jap. **10**, 143 (taken from Berg, *E. Coli in Motion*, Springer, 2004)

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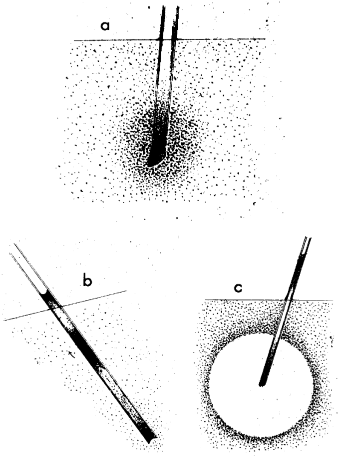

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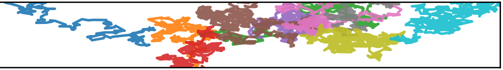

Experiments

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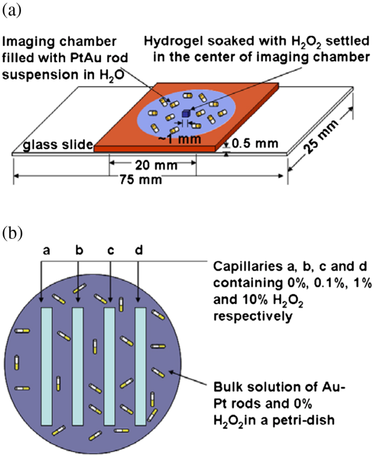

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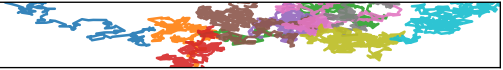

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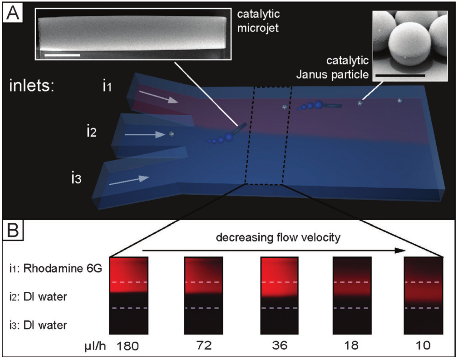

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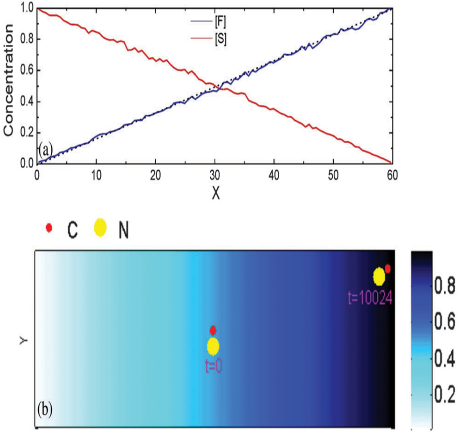

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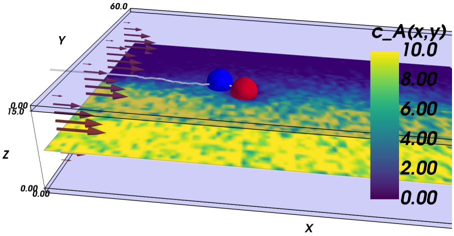
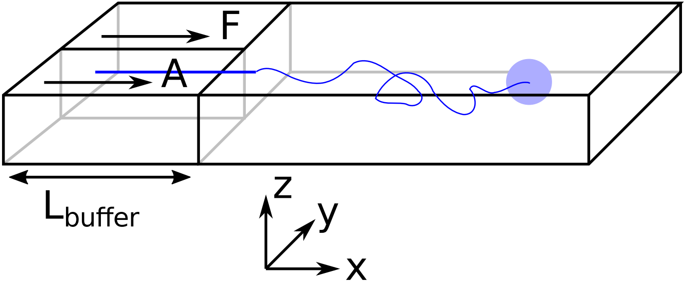


Mesoscopic simulation



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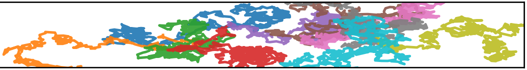


Force on the colloid

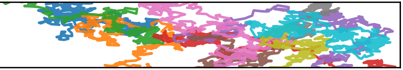
- Solve reaction-diffusion equation to obtain $c_\alpha(\vec{r})$
- Sum the contributions $-\Lambda_\alpha \frac{k_B T}{\eta} \nabla c_\alpha(\vec{r})$

Langevin equation for the sphere

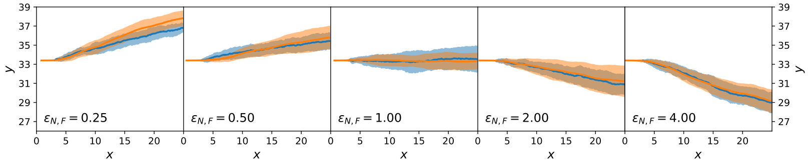
$$\dot{x} = v_{\mathrm{flow}} + \sqrt{2D}\xi_x$$

$$\dot{y} = \frac{F_y(x/v_{\mathrm{flow}}, y)}{\gamma} + \sqrt{2D}\xi_y$$

Chemotaxis

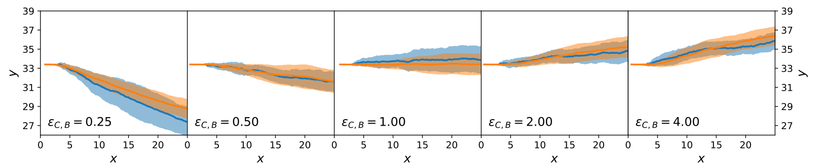


Passive sphere



Chemotaxis

Active sphere



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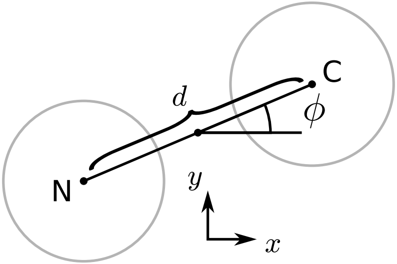

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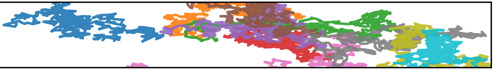
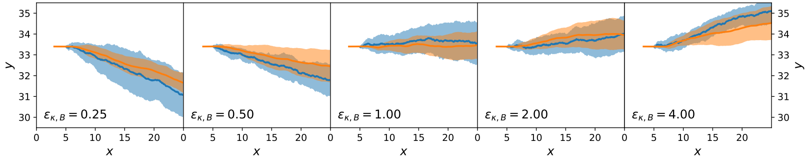
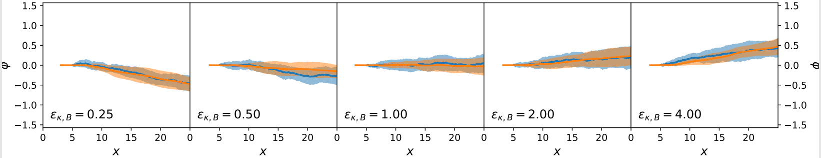


Dimer nanomotor





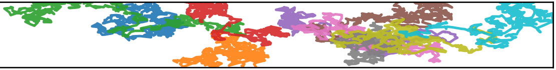
Chemotaxis

Active chemotaxis

- Langevin model to understand the chemotactic drift
- Translation and rotation → relate experimental drift to the relative magnitude of the Λ_α

Anisotropic nanomotors

Anisotropic nanomotors



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- ten Hagen *et al* (2014)

Simulations

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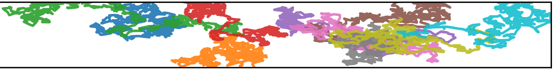

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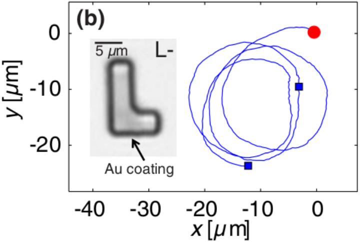

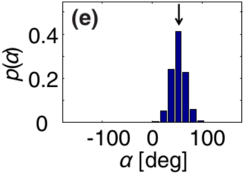

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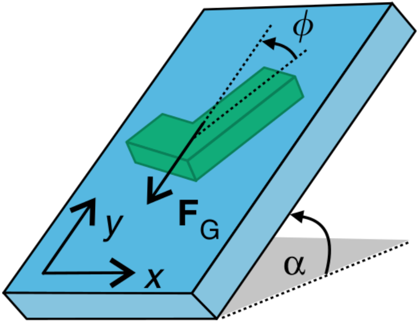

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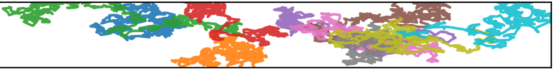

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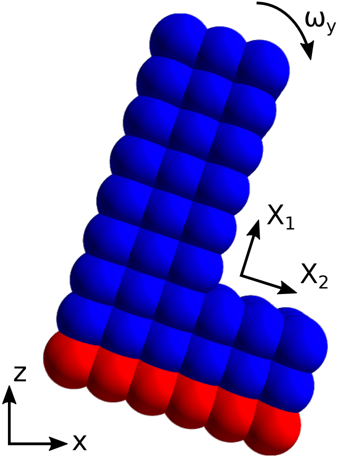

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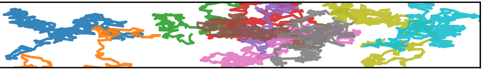
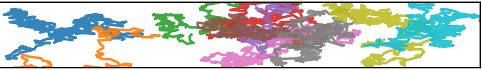


Stochastic model

$$\begin{pmatrix} \dot{X}_1 \\ \dot{X}_2 \\ \dot{X}_3 \end{pmatrix} = \sqrt{2D^L}\zeta + \beta D^L F \ ,$$

- D^L is the diffusion matrix
- ζ is a vector white noise
- F is an external force

Anisotropic nanomotors



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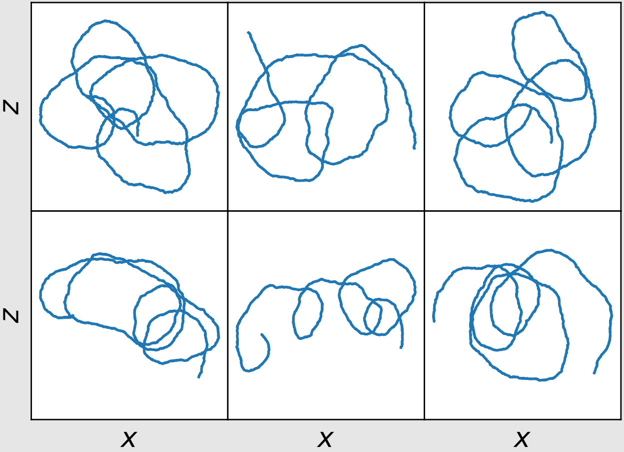
Hydrodynamics [Happel and Brenner (1983)]

1. Flow-induced self-propulsion
2. Hydrodynamic friction on all coupled degrees of freedom
3. (Also a direct torque)

Anisotropic nanomotors

Circling



Symmetry breaking

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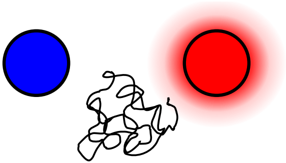
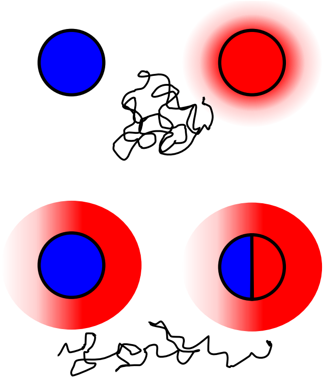


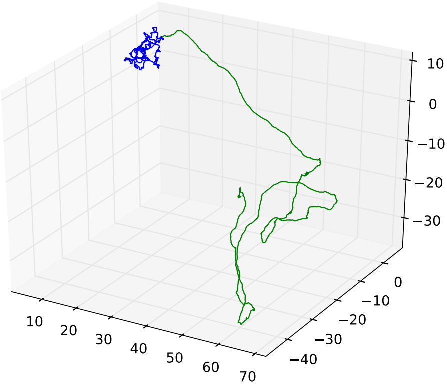
- Blue = passive Red = active

Symmetry breaking



- Blue = passive Red = active
- Functionalize specific sites of a colloid.
- Asymmetry → gradient generation.
- → self-propulsion.
- Basic operation of a chemical engine.

Symmetry breaking



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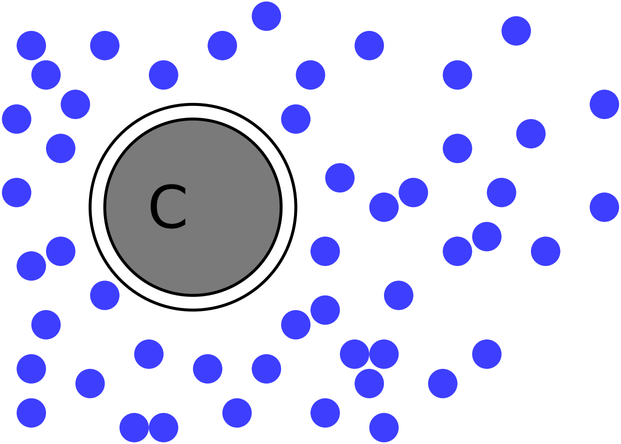

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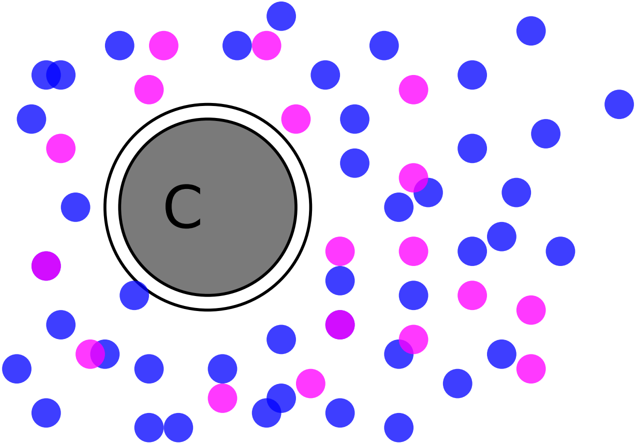

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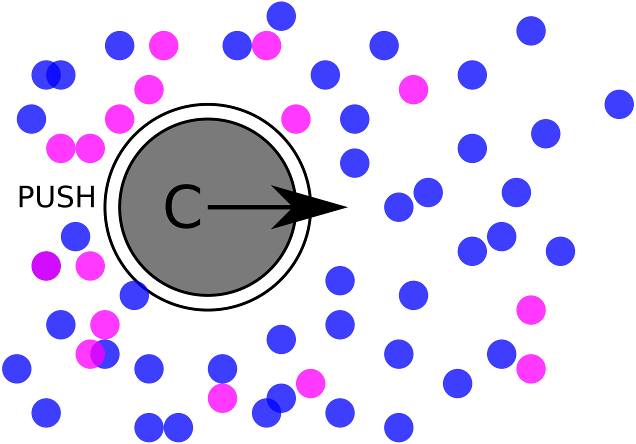

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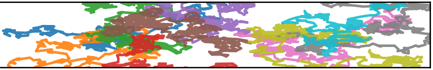
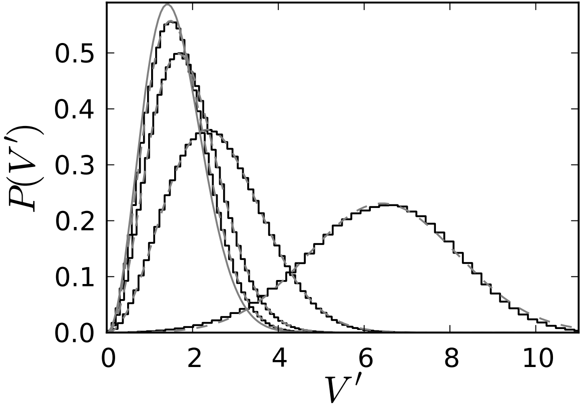


From left to right: $\sigma = 3, 5, 7$ and 9.



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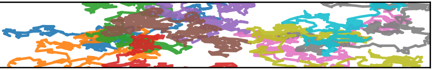

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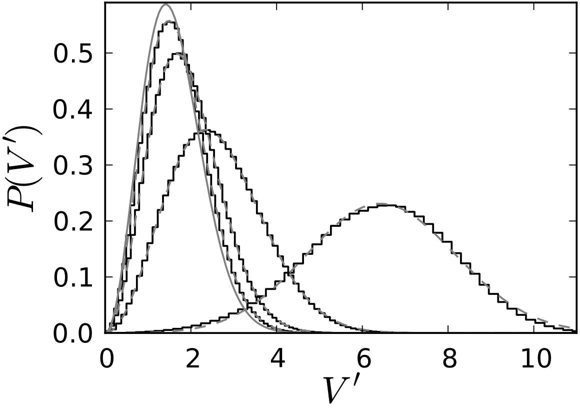

- Also: enhanced diffusion sub-treshold

Symmetry breaking

$$\partial_t n_B(\mathbf{r},t) = D\nabla^2 n_B(\mathbf{r},t) - k_2 n_B + \mathcal{S}(\mathbf{r},t).$$

- D is the diffusion coefficient of the fluid.
- k_2 is the bulk rate of the reverse reaction.
- $\mathcal{S}$ is the source term on the surface of the colloid that we approximate by a point source.
- Balancing against the friction, we obtain a condition for the threshold of the instability:

$$\mathcal{C} = \frac{4\pi}{3}\frac{k_B T}{\zeta}\frac{R_0^2}{D^2}\left(\Lambda_A - \Lambda_B\right) r_f\,,$$

when $\mathcal{C} = 1$. ζ is the friction coefficient and r_f the reaction rate per unit area.

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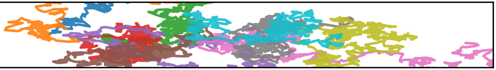
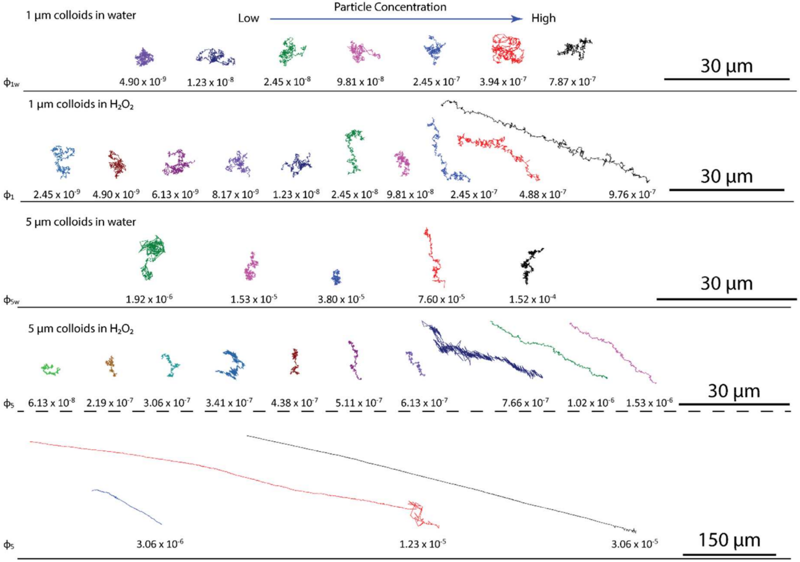
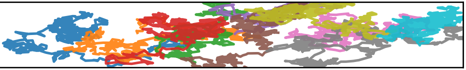
- In the units of the simulations, the critical radius of the particle is $\sigma \approx 4.7$.

Symmetry breaking



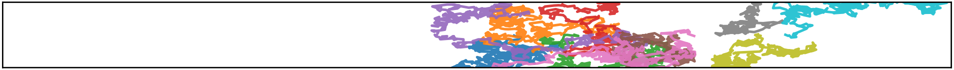


Symmetry breaking



Self-propulsion by symmetry breaking [de Buyl *et al* (2013)]

- Observation and rationale for the onset of self-propulsion by symmetry breaking
- Sub-treshold enhanced diffusion
- Recent experimental results confirming the phenomenon.



Perspectives

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Statistical physics

- Microscopic knowledge of all thermodynamic currents
- “Ideal” nonequilibrium device

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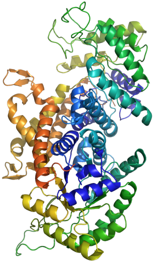
Biological machines - enzymes

- Experiments on *enhanced diffusion* and *directed migration*.
- Enhanced diffusion of chemically active enzymes



Perspectives

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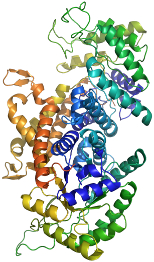

Thank you

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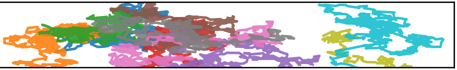

Introduction: what are nanomotors and why are they interesting?

Sedimentation

Chemotaxis

Anisotropic nanomotors

Symmetry breaking

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