Chemical motors: from single swimmers to collective effects

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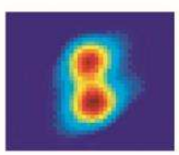

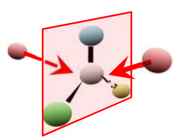

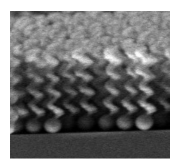

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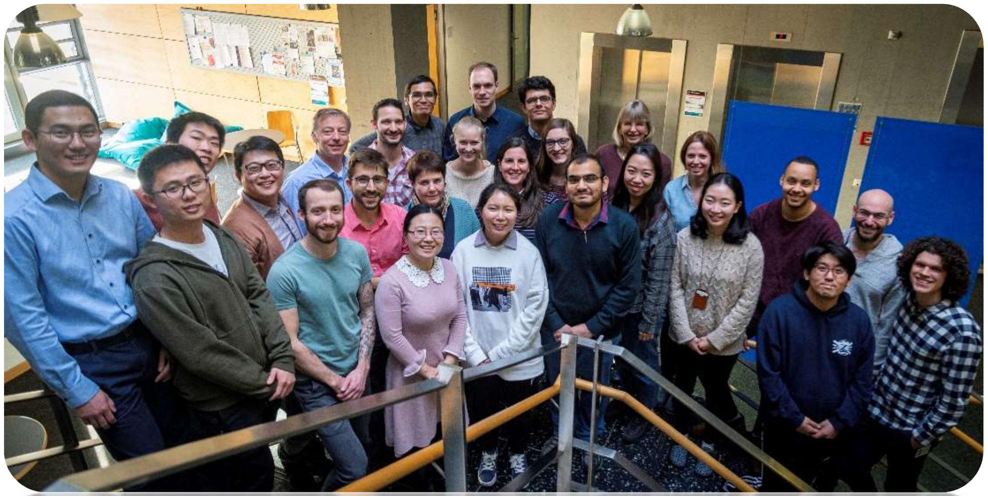

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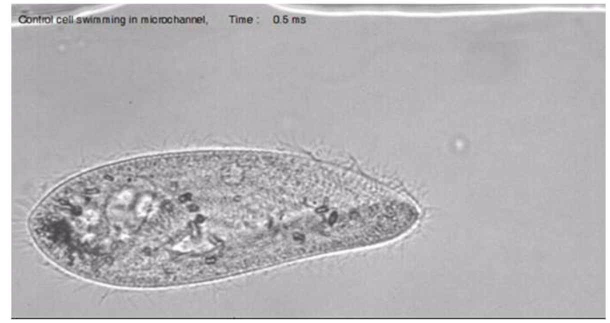
Swimming at different scales

Schooling Fish

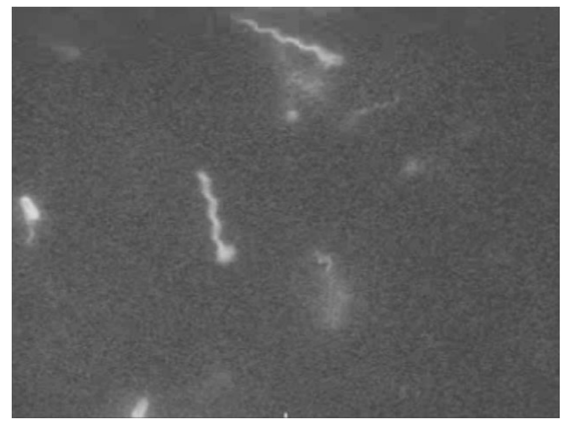
www.youtube.com/watch?v=Px81Y0e0icg

100.000 µm



100 µm

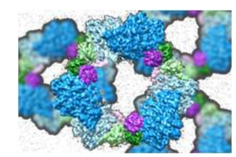
Integr. Biol., 2015

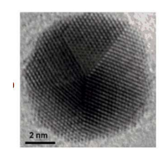


Linda Turner, Howard Berg, Rowland Inst Harvard

5 µm

Enzymes, Nanoparticles

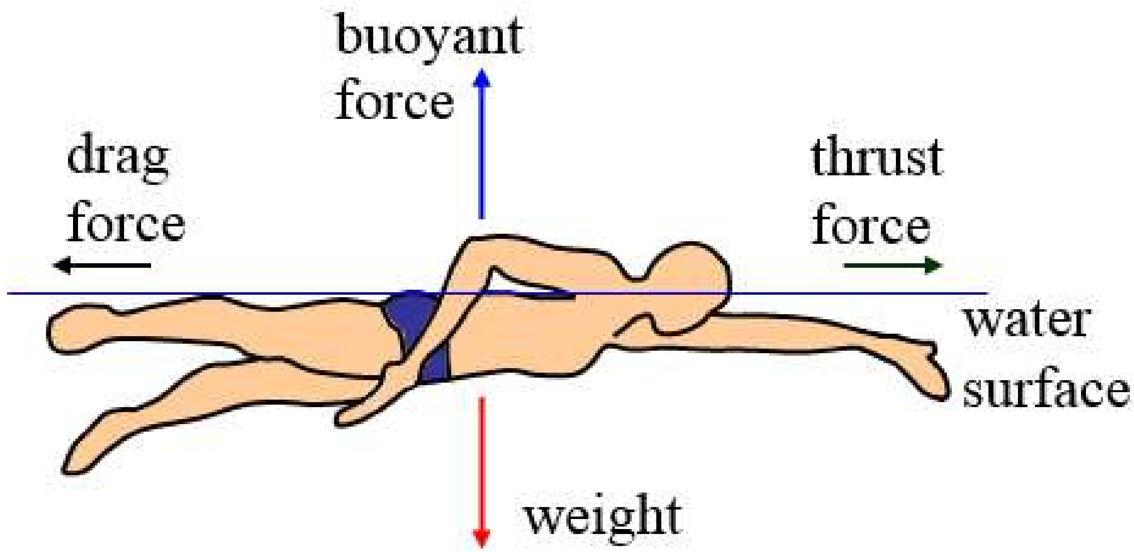




5 nm

1) ‘swimming’: move in liquid by deforming its body in a periodic way

2) forces are balanced



https://www.real-world-physics-problems.com/physics-of-swimming.html

Reynolds number

$$Re = \frac{\text{inertial force}}{\text{viscous force}} = \frac{\rho v L}{\eta}$$

Viscosity, η

water

syrup
(sugar solution)

https://www.youtube.com/watch?v=2Gdxu4XcsbY

Life at low Reynolds number

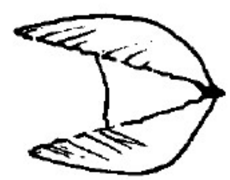
E. M. Purcell

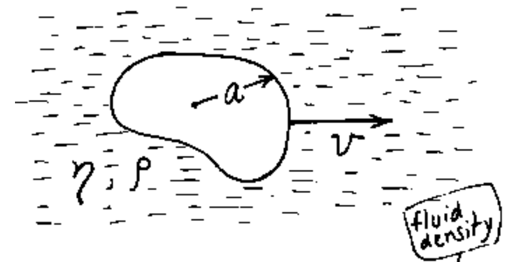
American Journal of Physics, Vol. 45, No. 1, January 1977

If $\mathcal{R} \ll 1$:

Time doesn't matter. The pattern of motion is the same, whether slow or fast, whether forward or backward in time.

The Scallop Theorem



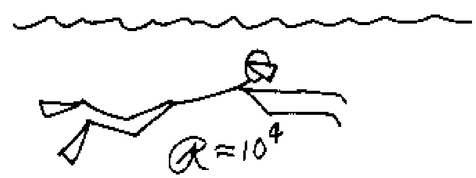


$$\frac{\text{inertial forces}}{\text{viscous forces}} \approx \frac{a v \rho}{\eta}$$

fluid viscosity

$$\mathcal{R} = \frac{a v \rho}{\eta} = \frac{a v}{\nu}$$

$\nu = 10^{-2}\ \text{cm}^2/\text{sec}$ for water



physicist‘s scallop

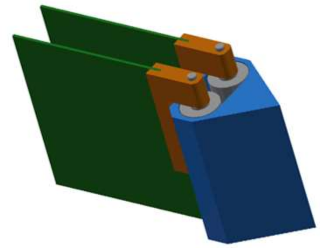
can this swim at micro-scale?

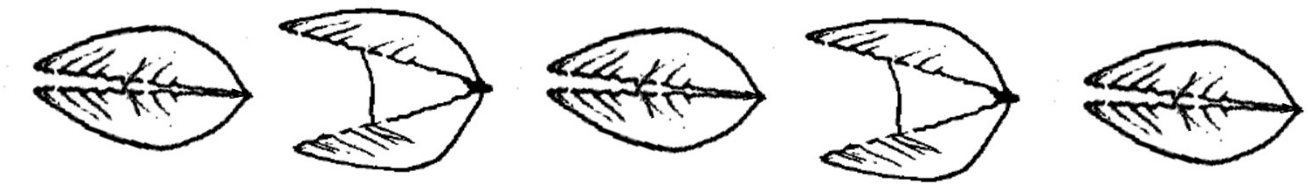
reciprocal motion

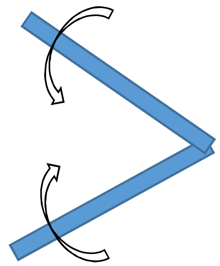
…A-B-A-B-A-B-A….

⟷

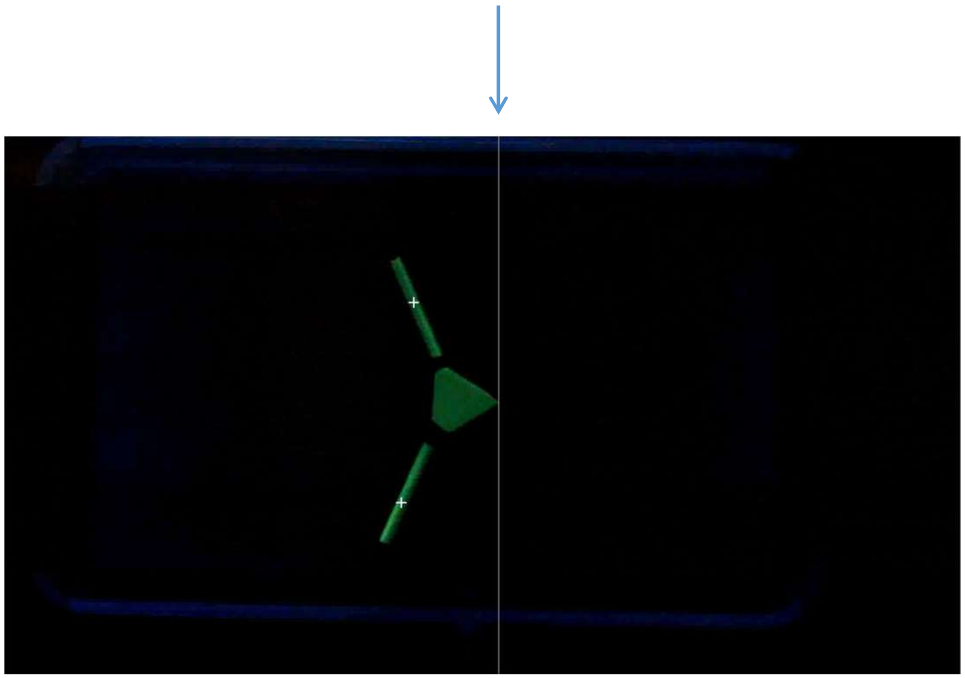
symmetric under time-reversal symmetry







Newtonian fluid
(silicone oil)



Re= 0.03 scallop theorem

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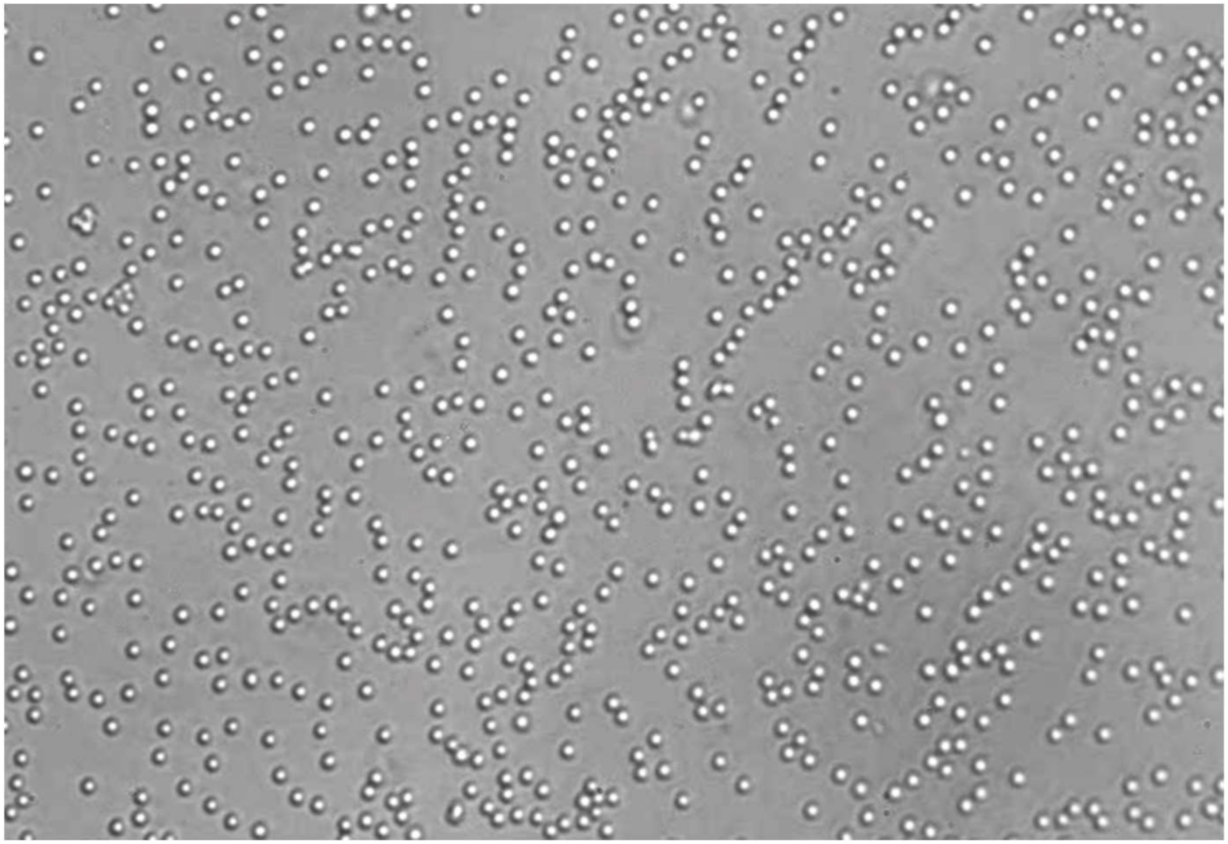
Chemical motors, chemical active matter

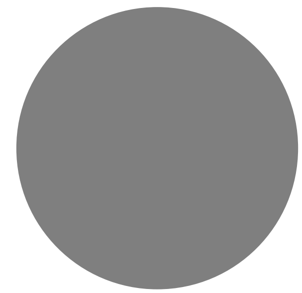
Microswimmers without body shape changes

Colloids – Brownian motion



1 μm
colloids

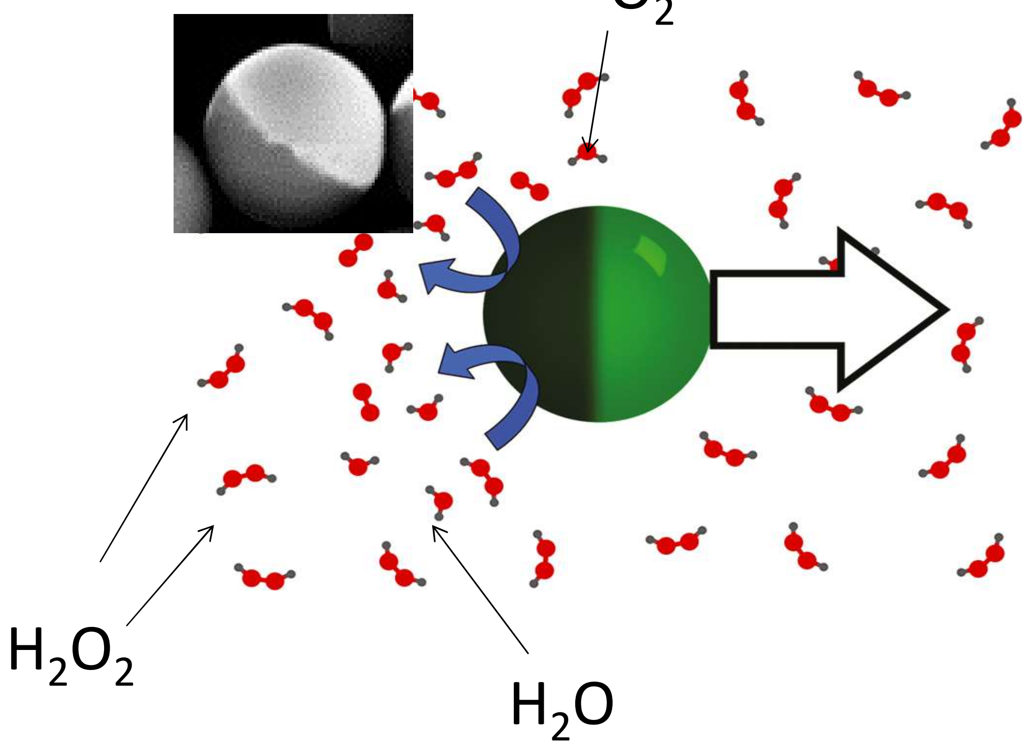
How to make them active:
Chemical nanomotors

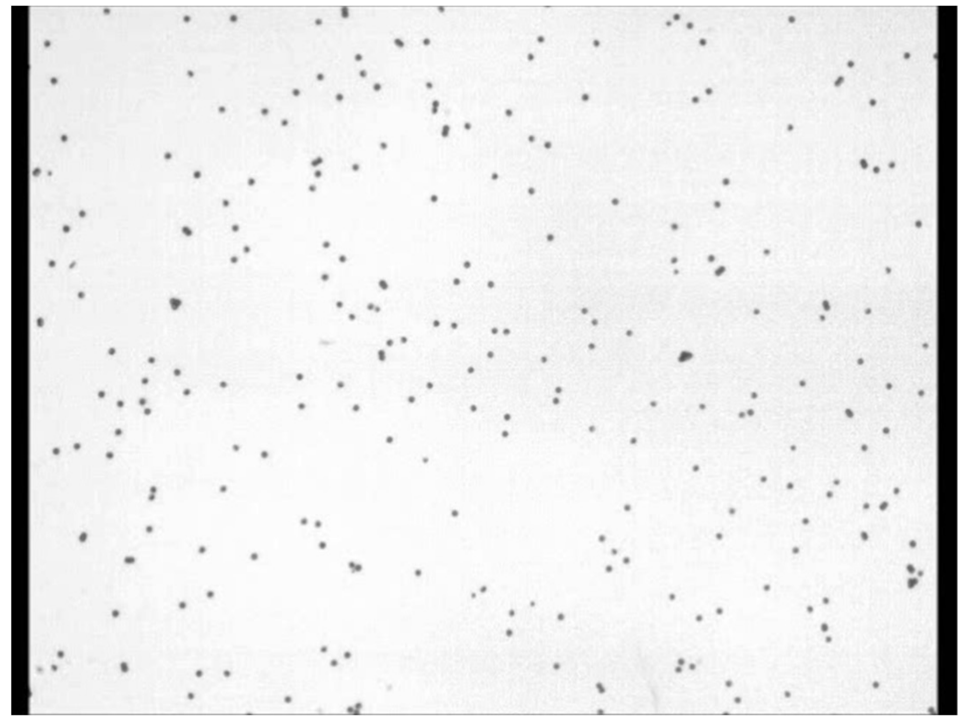


- needs an engine
- need to break symmetry

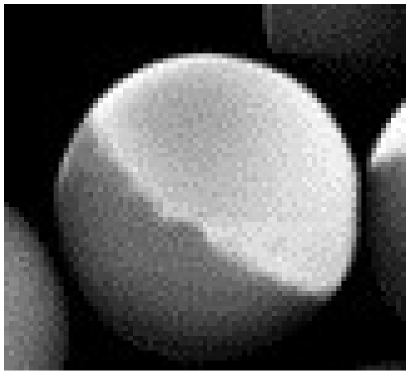
“Janus” Particle as chemical motor

$2H_2O_2 \rightarrow 2H_2O + O_2$

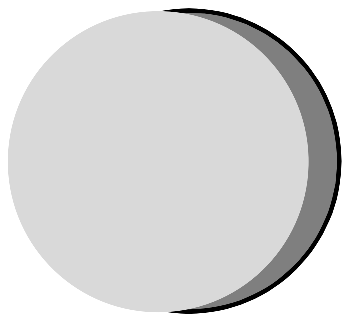


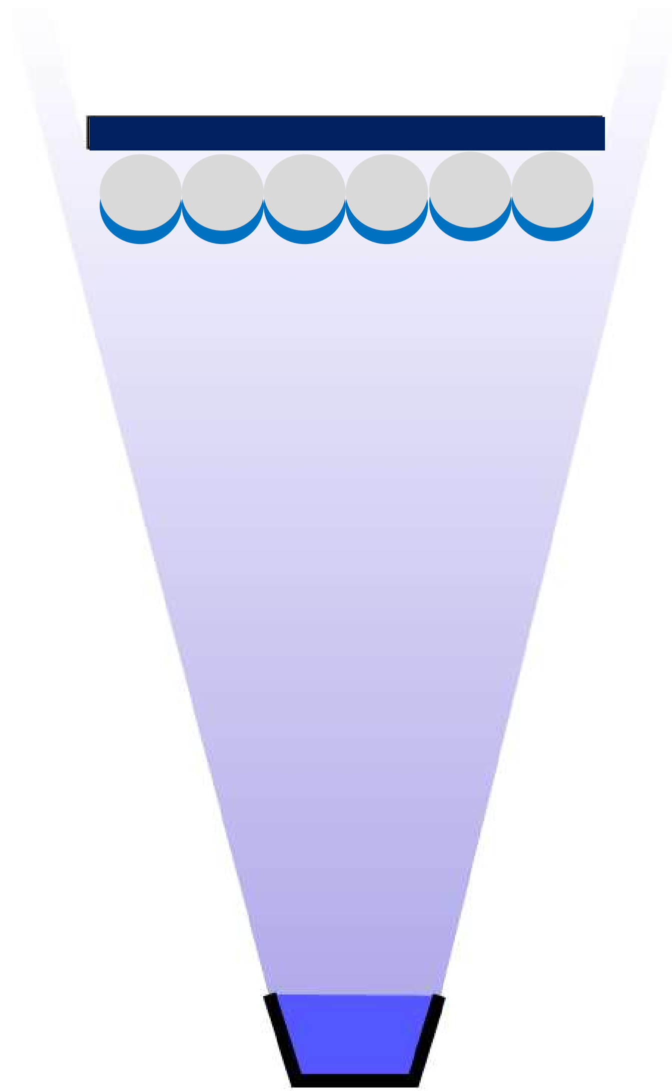


S. J. Ebbens and J. R. Howse, *Langmuir* 2011, **27**, 12293–12296

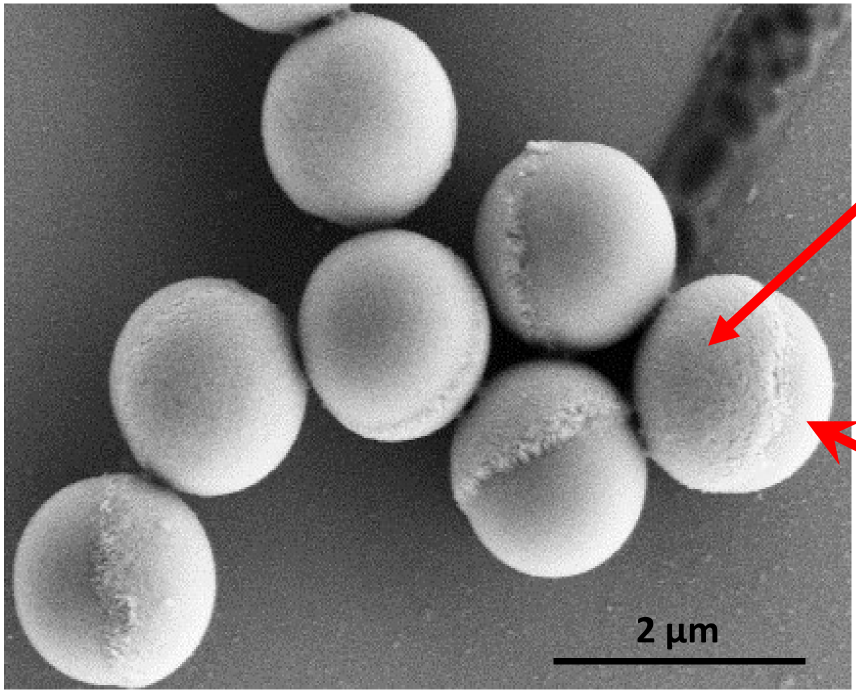


symmetry-broken
two-faced Janus particle





Janus particles



Catalytic-side ($Pt, TiO_{2,..}$)

Other side (PS, SiO_2)

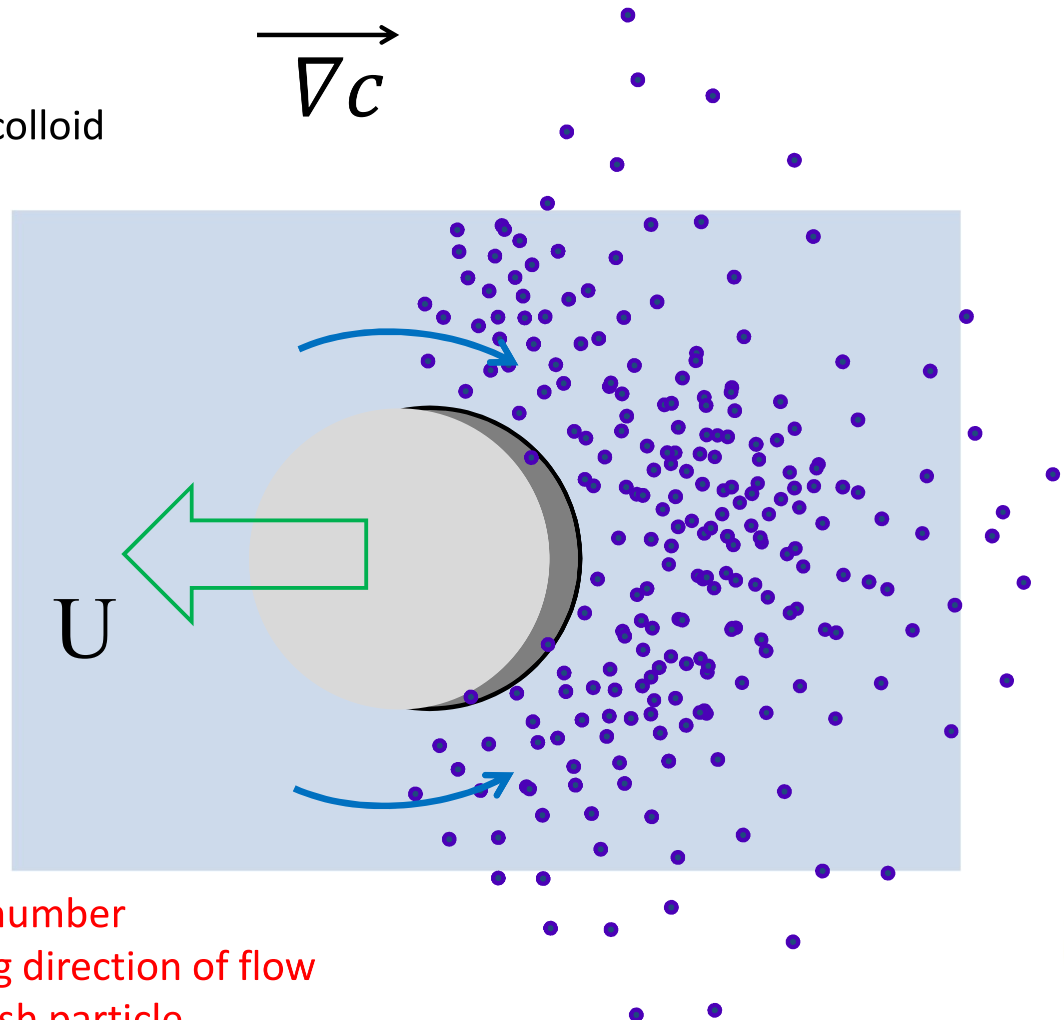
TiO_2-SiO_2 Janus particles (1.5 µm diameter)

Dhruv Singh

Self-phoretic

Self-diffusiophoretic colloid

„Chemical motor“



- At low Reynolds number
- No pressure along direction of flow
- Fluid does not push particle

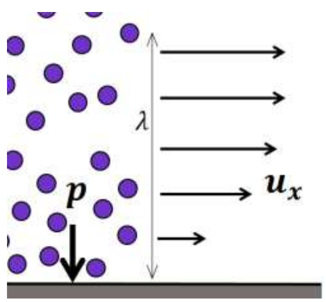
$$\vec{U} = \xi \frac{kT}{\eta} \vec{\nabla} c_{\text{ext}}$$

$$\frac{\partial p(x,z)}{\partial z} = -c(x,z)\,\frac{\partial \Phi(z)}{\partial z}, \qquad (1)$$

$$\frac{\partial p(x,z)}{\partial x} - \eta\,\frac{\partial^2 u_x(z)}{\partial z^2} = 0. \qquad (2)$$

$$c(x,z) = c_b(x)\,exp\left(\frac{-\Phi(z)}{k\,T}\right),$$

$$\frac{\partial p(x,z)}{\partial z} = -c_b(x)\,exp\left(\frac{-\Phi(z)}{k\,T}\right)\,\frac{\partial \Phi(z)}{\partial z}.$$



Integrate along z in zones z<λ to z> λ

$$p(x,z) = c_b(x)\,k\,T\,\left(e^{-\Phi(z)/(k\,T)} - 1\right).$$

Differentiate to be able to substitute in (2)

$$\frac{\partial p(x,z)}{\partial x} = \frac{\partial c_b(x)}{\partial x}\,k\,T\,\left(e^{-\Phi(z)/(k\,T)} - 1\right).$$

gives

$$\eta\,\frac{\partial^2 u_x(z)}{\partial z^2} = \frac{\partial c_b(x)}{\partial x}\,k\,T\,\left(e^{-\Phi(z)/(k\,T)} - 1\right).$$

Need to integrate twice along z for flow speed, depending on form of potential

$$\beta = \int\int \left(e^{-\Phi(z)/(k\,T)} - 1\right) dz\,dz,$$

Diffusio-osmotic flow speed

$$u_x = -\frac{\partial c_b(x)}{\partial x}\,\frac{k\,T}{\eta}\,\beta,$$

$$u_{\parallel} = -\nabla_{\parallel} c\,\frac{k\,T}{\eta}\,\beta,$$

We begin by noting that at low Reynolds number the flows must satisfy the Stokes equation (Eqn. 4.23), where we must now include the external force due to the interaction potential:

$$\vec{\nabla} p - \eta \nabla^2 \vec{u} = -c \vec{\nabla} \Phi, \tag{6.5}$$

and where we again assume that the fluid is incompressible, which is mathematically written as:

$$\vec{\nabla} \cdot \vec{u} = 0. \tag{6.6}$$

We can already see by inspection of Eqn. 6.5 that there must be a tangential flow along the wall. Since, the potential does not change along x, (i.e. $d\Phi/dx = 0$), but the pressure does, we can only have a change in pressure as a function of x in Eqn. 6.5, if the viscous term is nonzero. This must mean that the velocity along x cannot be zero. We now want to derive this result and an expression for the velocity.

We first consider the directional and functional dependence of the quantities shown in Fig. 6.1a. The pressure changes along x and z, i.e. $p(x, z)$, the velocity points along x and changes along z, i.e. $u_x(z)$, and similarly we see that $c(x, z)$, $\Phi(z)$, and $F_z(x)$. Substituting these terms into the Stokes vector equation (Eqn. 6.5) yields one expression for the z-component and one for the x-component:

$$\frac{\partial p(x,z)}{\partial z} = -c(x,z)\, \frac{\partial \Phi(z)}{\partial z}, \tag{6.7}$$

and

$$\frac{\partial p(x,z)}{\partial x} - \eta\, \frac{\partial^2 u_x(z)}{\partial z^2} = 0. \tag{6.8}$$

We can solve for the pressure in the Eqn. 6.7 and then use the result to solve for the flow speed in Eqn. 6.8. To do so, we need a functional form for the concentration. We assume that the change of the concentration of solute molecules as a function of distance from the surface is described by a Boltzmann distribution:

$$c(x,z) = c_b(x)\, exp\left(\frac{-\Phi(z)}{kT}\right), \tag{6.9}$$

where c_b is the concentration in the bulk (away from the surface of the colloid), $c_b(x) = c(x; z > \lambda)$. We can further assume that the interaction potential will be strong very close to the surface of the colloid and then quickly becomes negligible away from the colloid's surface. (Recall the scaling with distance of the van der Waals force, discussed in Chapter 1.) Substituting Eqn. 6.9 in Eqn. 6.7 gives:

$$\frac{\partial p(x,z)}{\partial z} = -c_b(x)\, exp\left(\frac{-\Phi(z)}{kT}\right)\, \frac{\partial \Phi(z)}{\partial z}. \tag{6.10}$$

We can now integrate both sides of the equation with respect to z. As is seen in Fig. 6.1, λ divides an inner zone ($z < \lambda$) where the interaction potential is strong from the outer zone ($z \geq \lambda$), where the potential is assumed to play no role. The limits of integration are chosen to match the pressures near this transition zone. Furthermore, the pressure far away from the surface must be equal to the pressure in the bulk. The latter can be set to zero (as we are interested in pressure changes). This means that the function is integrated from $z < \lambda$ to $z \geq \lambda$, which gives:

$$p(x,z) = c_b(x)\, kT\, \left(e^{-\Phi(z)/(kT)} - 1\right). \tag{6.11}$$

To be able to substitute the result into Eqn. 6.8, we first need to differentiate Eqn. 6.11 with respect to x:

$$\frac{\partial p(x,z)}{\partial x} = \frac{\partial c_b(x)}{\partial x}\, kT\, \left(e^{-\Phi(z)/(kT)} - 1\right). \tag{6.12}$$

Substitution into Eqn. 6.8 then gives

$$\eta\, \frac{\partial^2 u_x(z)}{\partial z^2} = \frac{\partial c_b(x)}{\partial x}\, kT\, \left(e^{-\Phi(z)/(kT)} - 1\right). \tag{6.13}$$

This equation needs to be integrated twice along z, to obtain the flow speed u_x. The difficulty is that we do not know the precise form and functional dependence of the potential $\Phi(z)$, which is the only term that we need to consider in the integration, as the other terms are constants or depend on x. Depending on the form of the potential one assumes, one can write the result of the double integration as:

$$\beta = \int\int \left(e^{-\Phi(z)/(kT)} - 1\right) dz\, dz, \tag{6.14}$$

such that the speed of the diffusioosmotic flow near the surface is:

$$u_x = -\frac{\partial c_b(x)}{\partial x}\, \frac{kT}{\eta}\, \beta, \tag{6.15}$$

and more generally

$$u_{\parallel} = -\nabla_{\parallel} c\, \frac{kT}{\eta}\, \beta, \tag{6.16}$$

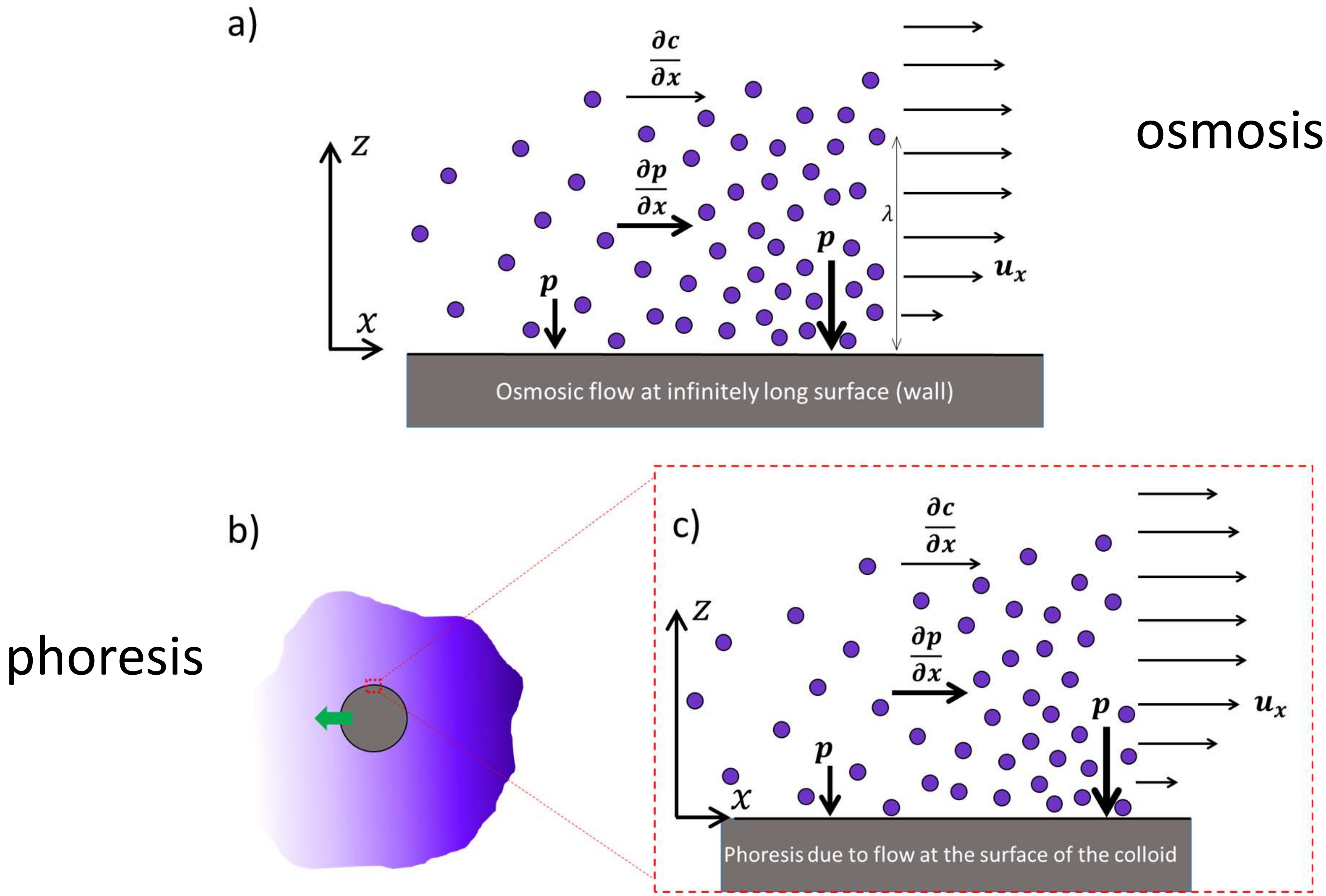
where $u_{\parallel}$ indicates the tangential flow direction. In the Figure it is along x, but in general it is parallel to the surface. It is seen that the diffusioosmotic flow is a function of temperature, the viscosity, and that it depends on the concentration gradient along the surface of the colloidal particle.

What is special about osmosis? It is interesting that a steady fluid flow parallel to a wall emerges at low Reynolds number, even though no external pressure difference is applied, or any forces are applied to the fluid in the direction parallel to the wall, where the flow is seen.

6.2.2 Phoresis

We have established that a concentration gradient parallel to the surface $\nabla_{\parallel} c$ causes a flow along the surface. For the fluid to be able to move along the surface of the colloid, here from left to right (see Fig. 6.1), 'it needs space' on the right, as the liquid cannot be compressed. The space is generated by the particle moving in the opposite direction (to the left) to make space on the right. This is known as the phoretic motion of the colloid, which is obtained by integrating the flow across the entire surface of the colloid (with has a radius R). The particle moves with speed U in the opposite direction to the integrated diffusioosmotic flow:

$$U = -\frac{1}{4\pi R^2} \int_{surface} u_{\parallel}\, dS, \tag{6.17}$$


a)
osmosis
Osmosic flow at infinitely long surface (wall)
b)
phoresis
c)
Phoresis due to flow at the surface of the colloid
$\frac{\partial c}{\partial x}$
$\frac{\partial p}{\partial x}$
p
u_x
λ
z
x

Diffusio-osmotic flow speed

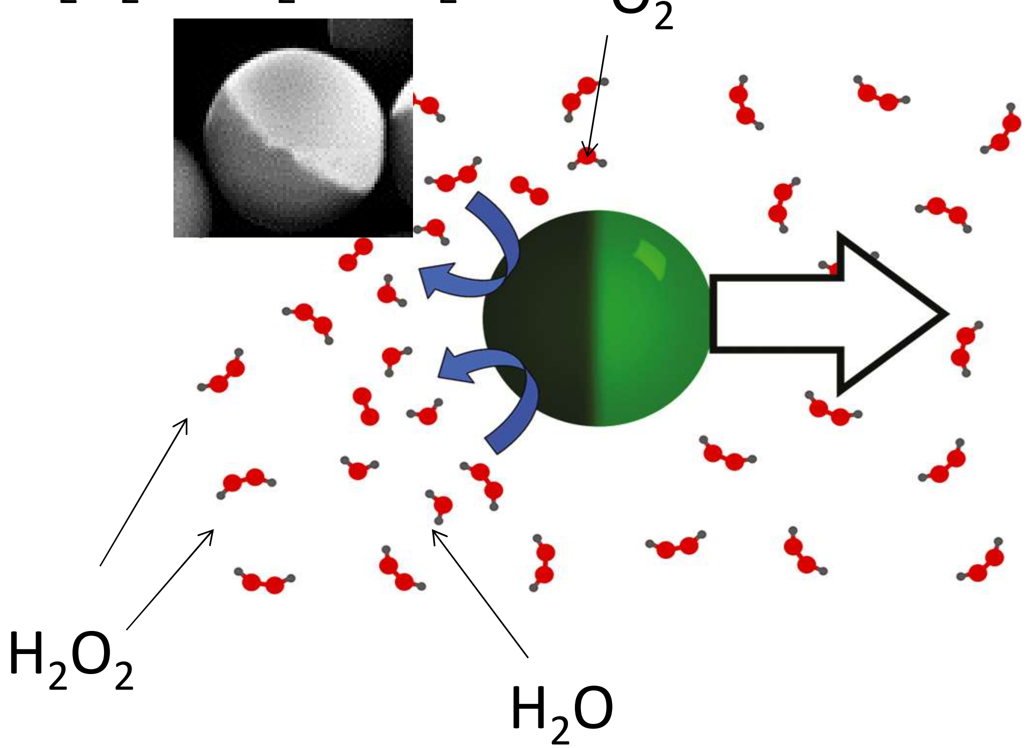
$$u_{\|} = -\nabla_{\|} c \, \frac{kT}{\eta} \, \beta,$$

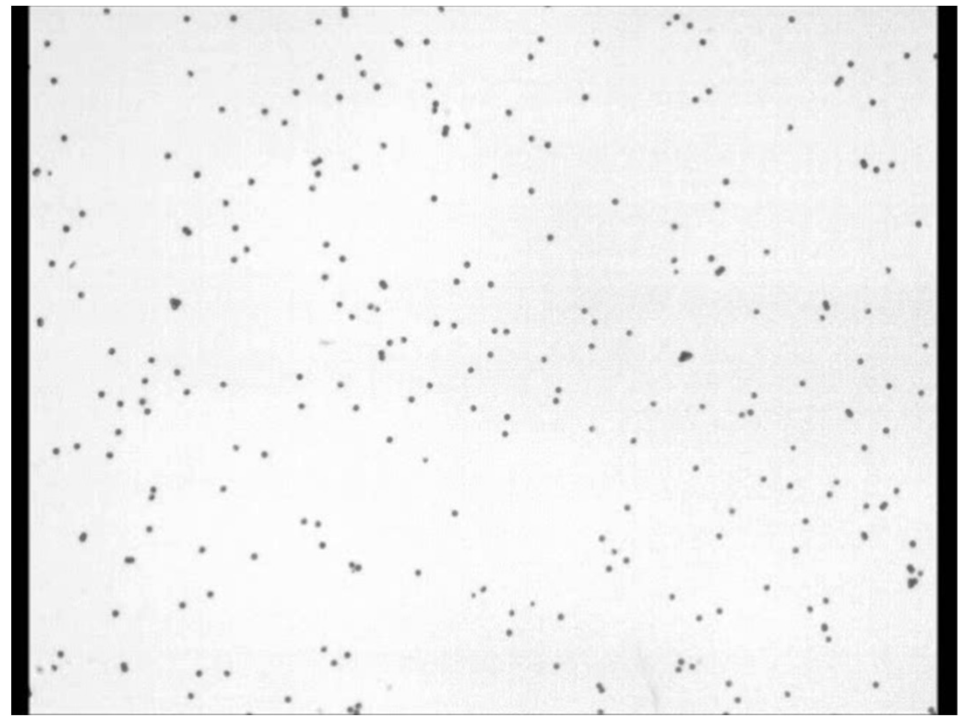
Particle moves with speed U in the opposite direction to the integrated diffusio-osmotic flow

$$U = -\frac{1}{4 \pi R^2} \int_{surface} u_{\|} \, dS,$$

“Janus” Particle as chemical motor

$2H_2O_2 \rightarrow 2H_2O + O_2$





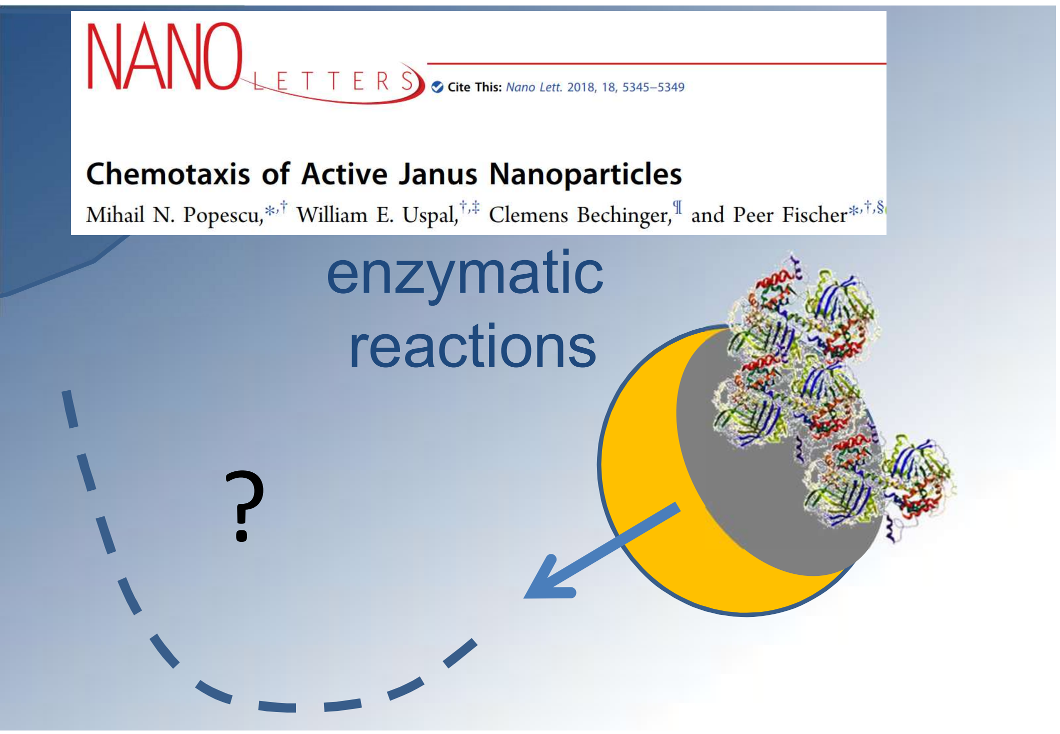
S. J. Ebbens and J. R. Howse, *Langmuir* 2011, **27**, 12293–12296

Chemotaxis

Active Brownian particles – current research:

active enzyme-powered nanocarriers

as active matter

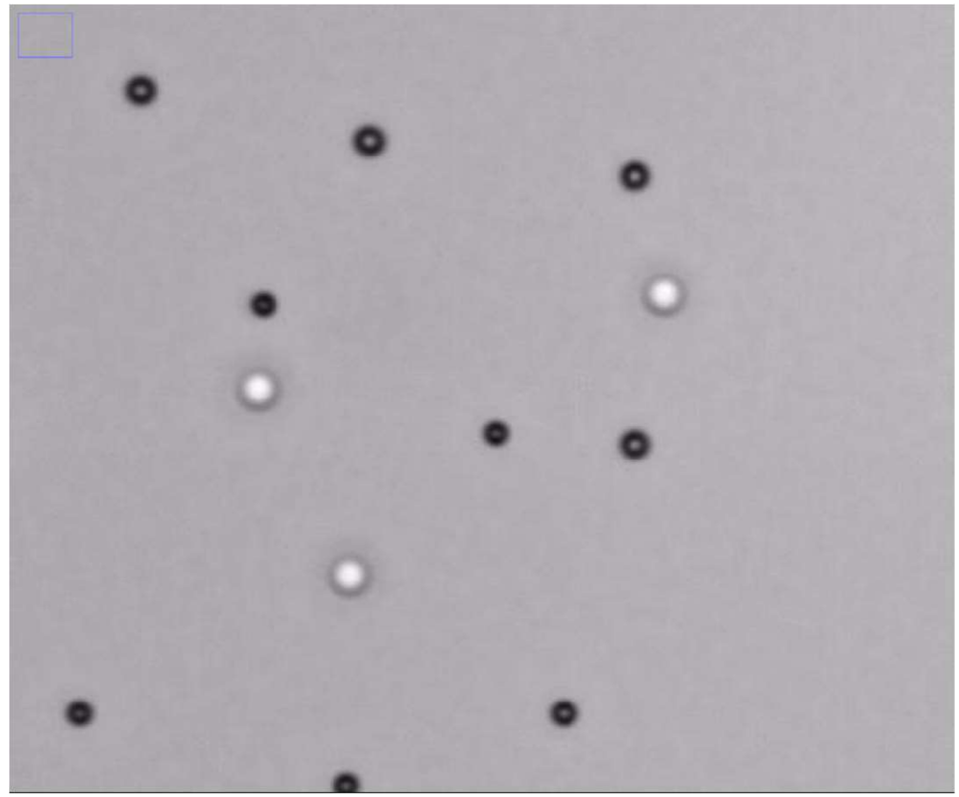


www.youtube.com/watch?v=QOGCSBh3kmM

Collective effects

Demonstration of spontaneous symmetry breaking in reactive colloids

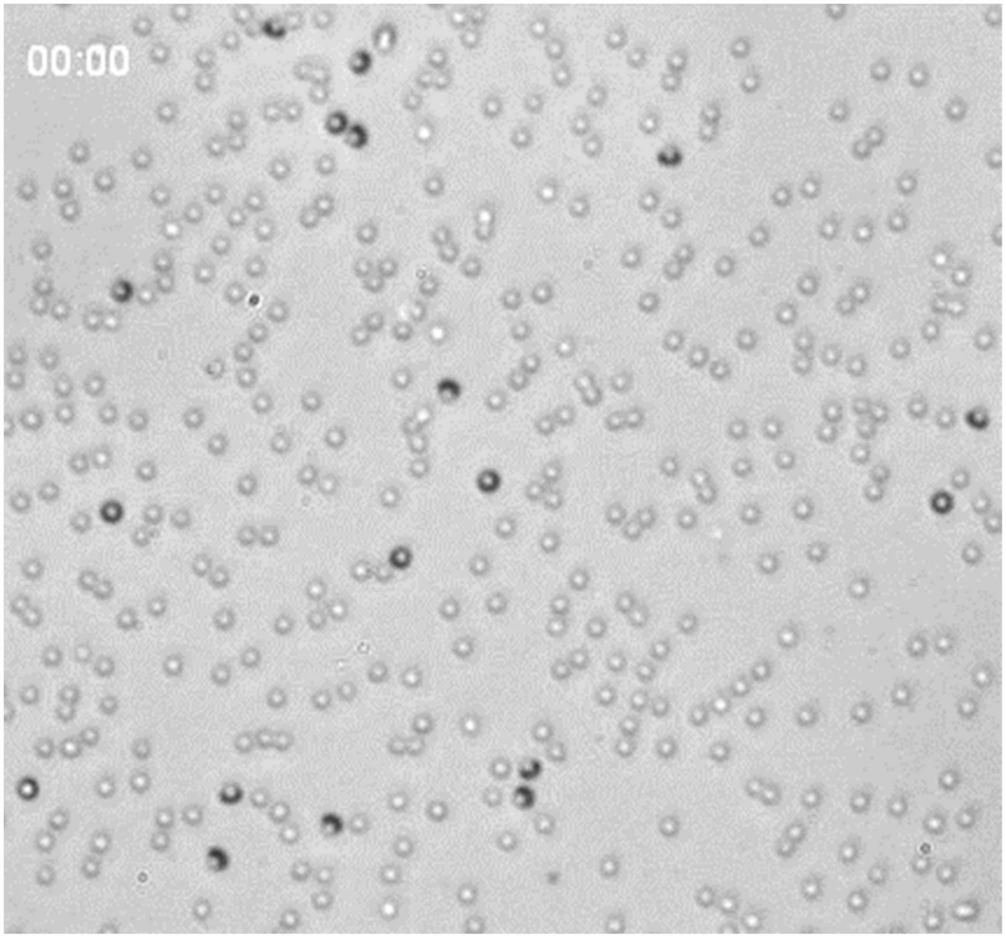
- white colloids not reactive
- on surface of dark a chemical reaction takes place
- dark colloids create a chemical field
- concentration gradient that attracts the white colloids)
- together they form a structure that is no longer symmetric and can propel



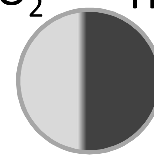
activity & hydrodynamics

***Chem. Comm.* 54**, 11933 (2018)

Active TiO_2 with SiO_2 Colloids

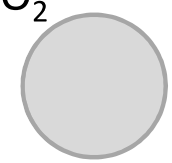


SiO_2 TiO_2



Active particles
Surface fraction 0.4%

SiO_2



Plain silica particles

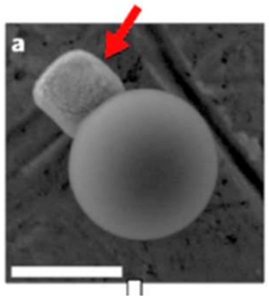
Surface fraction 8%

- TiO_2-SiO_2 Janus particles (1.5 µm) + SiO_2 particles (1.5 µm)
- 7 pH solution (1.5 % H_2O_2)

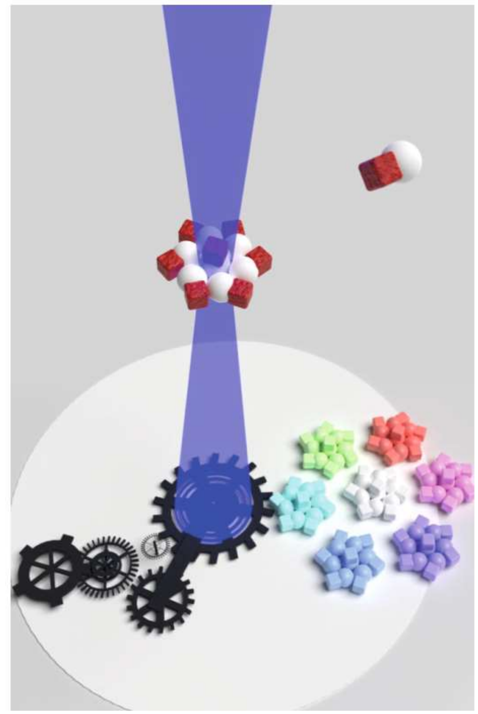
Adv. Mat. **29**, 1701328 (2017)

ACTIVE MATTER

A machine from machines



Colloidal particle with catalyst



- Microparticles
- Chemical reactions
- Hydrodynamics, concentration fields

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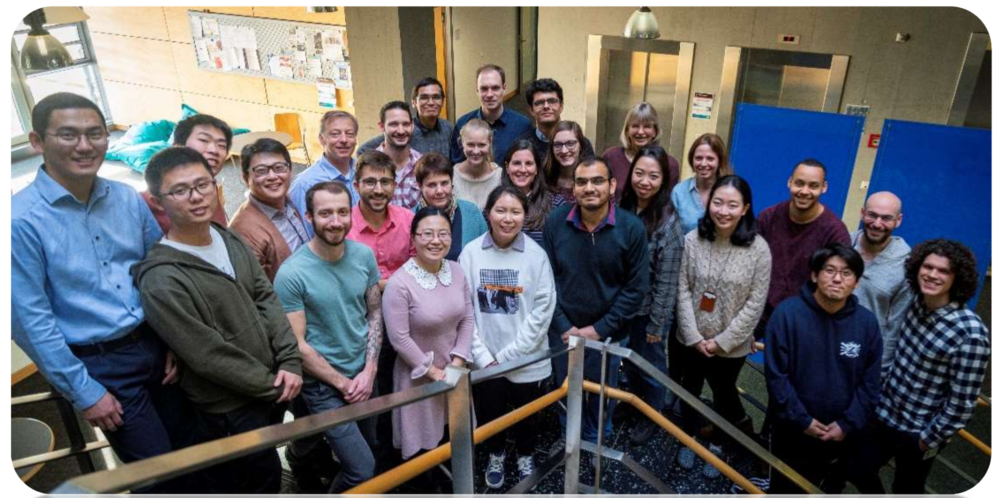

Thank you for your attention!

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