Active Colloidal Swimmers

as building blocks for **active matter**

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Active Colloids

Questions we would like to address:

- How can we make colloids active?
- How will their behaviour differ from passive colloids?
- What happens when we put them together and they interact?
- Could we design dead swimmers who can exhibit the same behaviour as living swimmers?

Non-equilibrium Transport: Phoretic Motion

- Electrophoresis

  Smoluchowski (1903)

- Thermophoresis

  Ludwig (1856), Soret (1879)

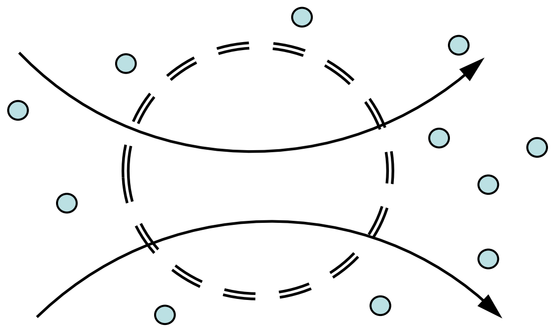
- Osmophoresis

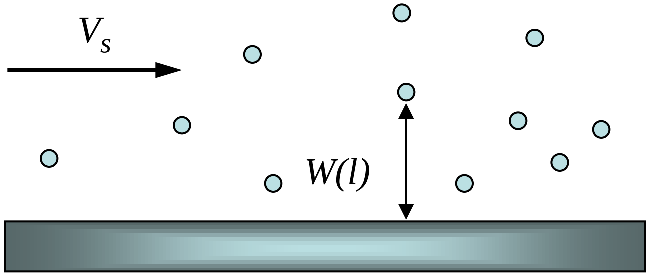
  Sackmann *et al* (1999)

- Diffusiophoresis

  Derjaguin *et al* (1961),

  Anderson & Prieve (1984)

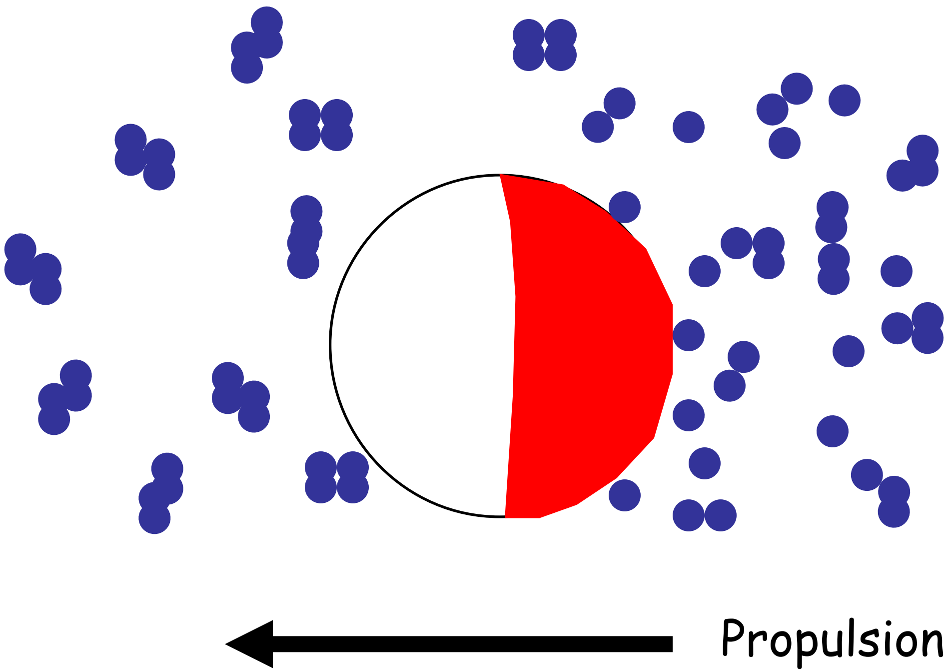




Phoretic Transport is Force-Free

Propulsion via Self-Phoresis

e.g. self-diffusiophoresis



Chemical reaction produces more products than reactants

Propulsion (repulsive interaction)

Particle half-coated with catalyst

R. Golestanian, T. Liverpool & A. Ajdari (2005)

Analysis of the Motion

- Slip Velocity

$$\mu = k_{\mathrm{B}}T\lambda^2/\eta$$

$$\lambda_D^2 = \int_0^\infty dl\ l\left[1 - \mathrm{e}^{-W(l)/k_{\mathrm{B}}T}\right]$$

$$\mathbf{v}_{\mathrm{s}}(\mathbf{r}_{\mathrm{s}}) = \mu(\mathbf{r}_{\mathrm{s}})(\mathbf{I} - \mathbf{nn}) \cdot \nabla c(\mathbf{r}_{\mathrm{s}})$$

- Source at the Surface

$$D\nabla^2 c = 0$$

$$-D\mathbf{n} \cdot \nabla c(\mathbf{r}_{\mathrm{s}}) = \alpha(\mathbf{r}_{\mathrm{s}})$$

mobility

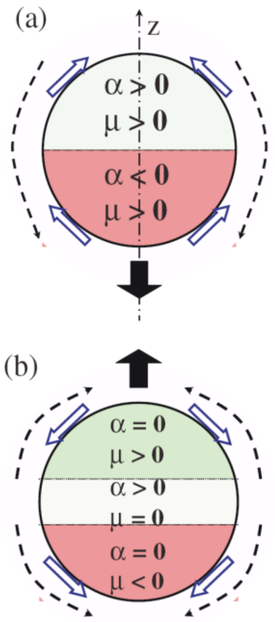
activity

Propulsion via Self-Phoresis

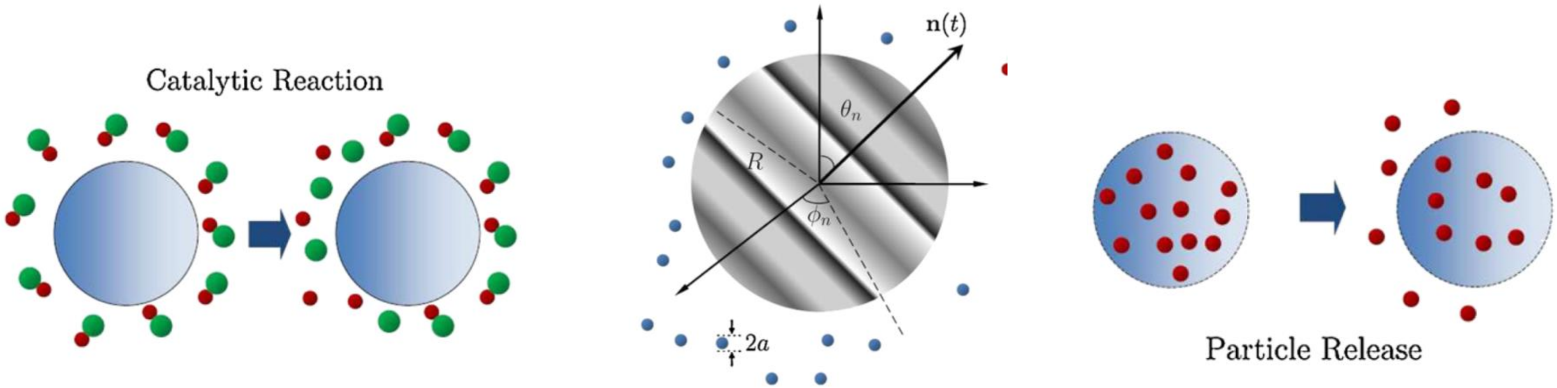
- Swimming Velocity

$$V \sim \alpha\mu / D$$

- Design-related Questions
  - Symmetry breaking
  - Relative importance of activity/mobility
  - Effect of Geometry
- Generic for Any Phoresis



Stochastic Dynamics of Phoretic Swimmers

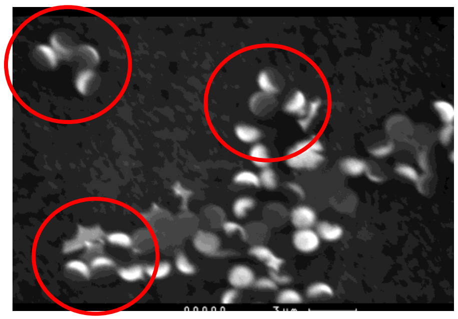


Asymmetric Contribution	$\sim t^2$ *inertial*	$\sim t^2$ *propulsive*	$\sim t^2 - \gamma\, t^{3/2}$ *propulsive + anomalous*	$\sim t$ *diffusive*
Symmetric Contribution	$\sim t^2$ *inertial*	$\sim t^{3/2}$ *anomalous*	$\sim t$ *diffusive*	
Hydrodynamic Contribution	$\sim t^2$ *inertial*	$\sim t - \beta\, t^{1/2}$ *diffusive + anomalous*		

τ_h τ_d τ_r

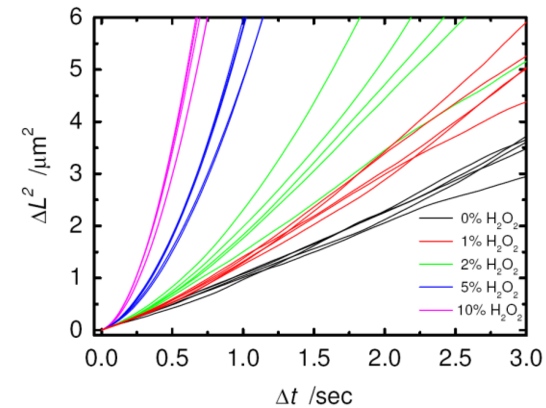
R. Golestanian (2009)

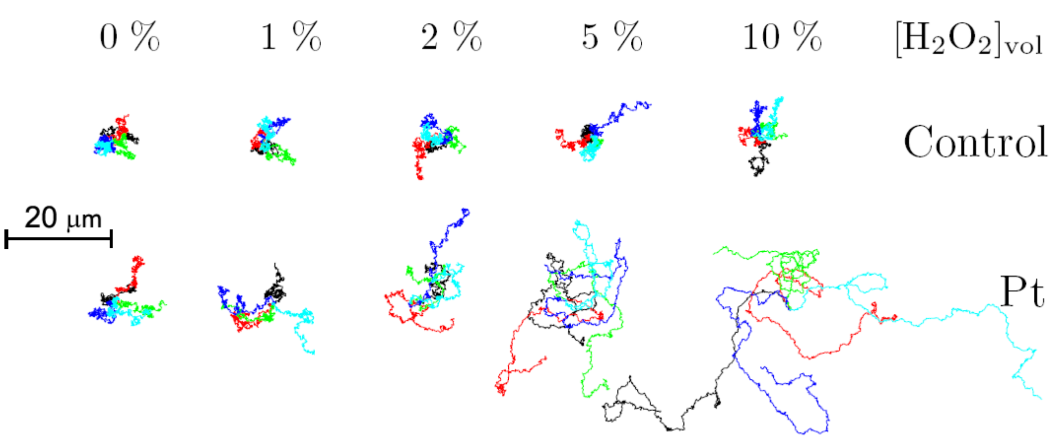
Experiments on Self-Phoresis



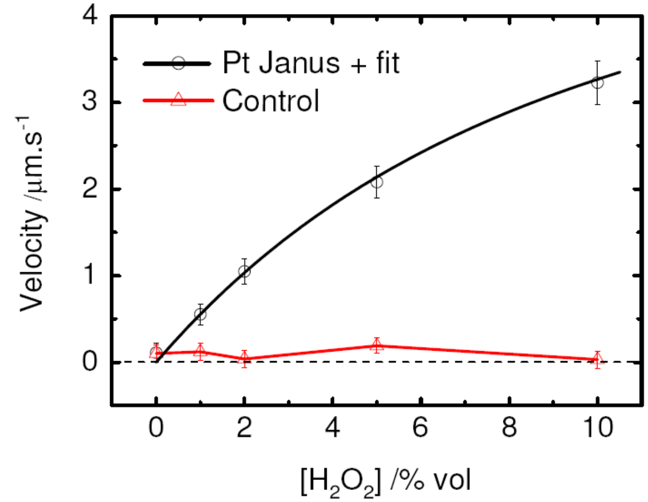
half-Pt coated spherical
PS beads in aqueous
hydrogen peroxide solution

Ebbens et al (2010)





Howse et al (2007)



Outline of My Talk

I. Self-Assembled Active "Molecules" in Dilute Heterogeneous Mixtures of Symmetric Colloids

II. Collective Chemotaxis of Asymmetric Active Colloids: the appearance of Debye screening, and various forms of instability

III. Self-Organised Swarms in light-activated thermally active symmetric colloids that exhibit phototaxis

Part I

Chemical Activity

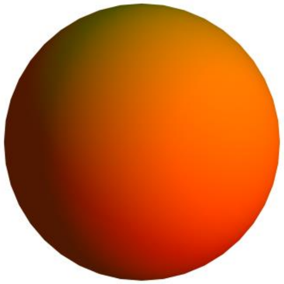
… Self-Assembled Active 'Molecules" …

Active Colloidal Molecules

Source or Sink of Chemicals: $C(r) \sim \alpha R^2/(Dr)$

Analogous to **Coulomb** or **Gravitational** potential

Two active colloids: it's complicated!



$$\vec{V}_1 \sim -\alpha_2 \mu_1 \frac{R^2 \vec{r}_{12}}{D|\vec{r}_{12}|^3}$$

$$\vec{V}_2 \sim \alpha_1 \mu_2 \frac{R^2 \vec{r}_{12}}{D|\vec{r}_{12}|^3}$$

Action ≠ Reaction

R. Soto & R. Golestanian (2014)

Active Self-Assembly

Brownian dynamics simulation:

$$\frac{d\vec{r}_i}{dt} = \sum_{k \neq i} \frac{\alpha_k \mu_i R^2}{6\pi D} \frac{\vec{r}_{ik}}{|\vec{r}_{ik}|^3} + \vec{\xi}_i(t) = V_0 \sum_k \widetilde{\alpha}_k \widetilde{\mu}_i \frac{\sigma^2 \vec{r}_{ik}}{|\vec{r}_{ik}|^3} + \vec{\xi}_i(t)$$

+excluded volume effect.

Colloidal molecules spontaneously form via self-assembly, and exhibit different types of activity depending on **symmetry**

Two types of colloids for simplicity, with different valences:

A  $\widetilde{\alpha}_A \geq 1 \qquad \widetilde{\mu}_A \geq 0$

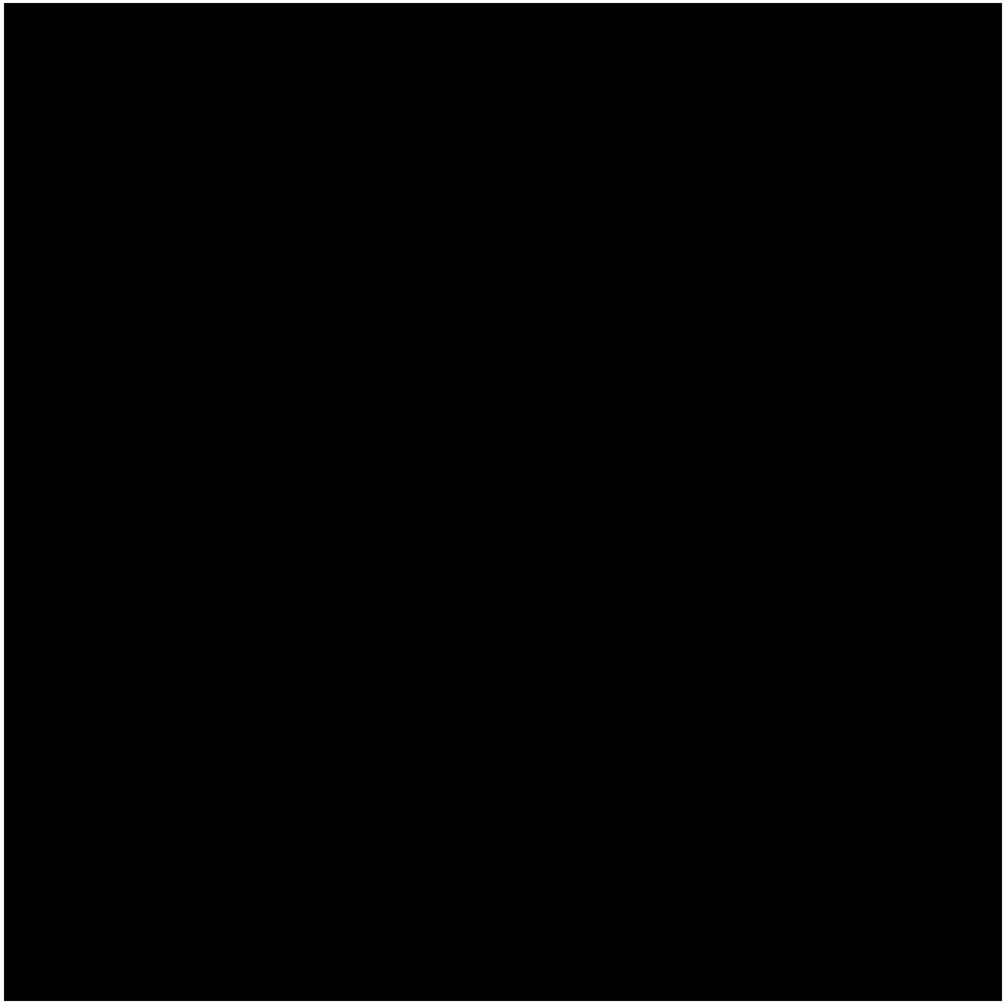
B  $\widetilde{\alpha}_B = \widetilde{\mu}_B = -1$

AB, AB_2, AB_3, … , AB_n

A 

$\widetilde{\alpha}_A = 3$

$\widetilde{\mu}_A = 0$



B 

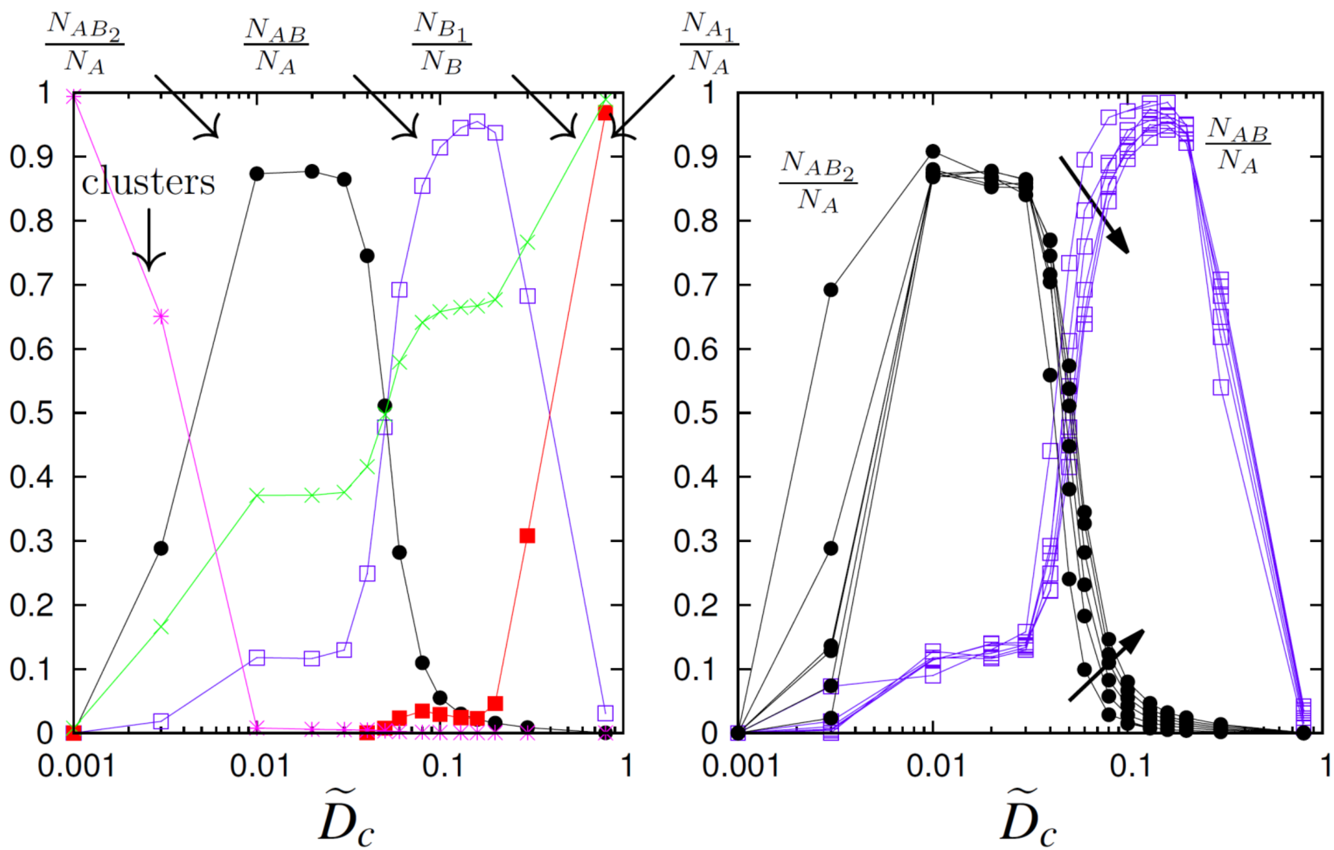
$\widetilde{\alpha}_B = \widetilde{\mu}_B = -1$

Molecular Populations vs Temperature

A  $\widetilde{\alpha}_A = 3 \quad \widetilde{\mu}_A = 0$

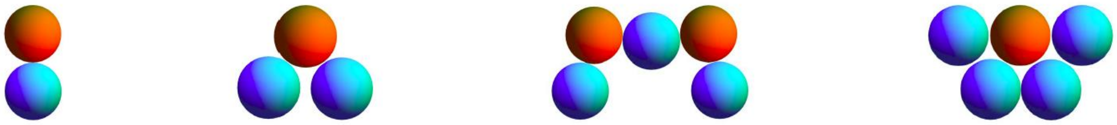
B  $\widetilde{\alpha}_B = \widetilde{\mu}_B = -1$

Stable molecules are not necessarily "charge neutral"

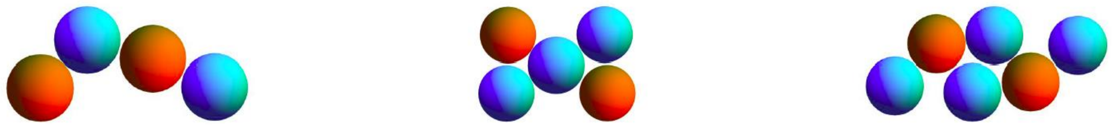


Tabulating Active Molecules

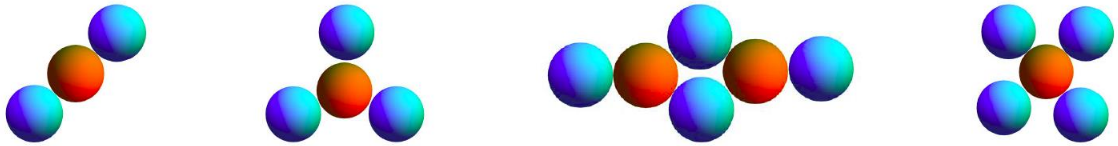
Translational propulsion



Rotational propulsion

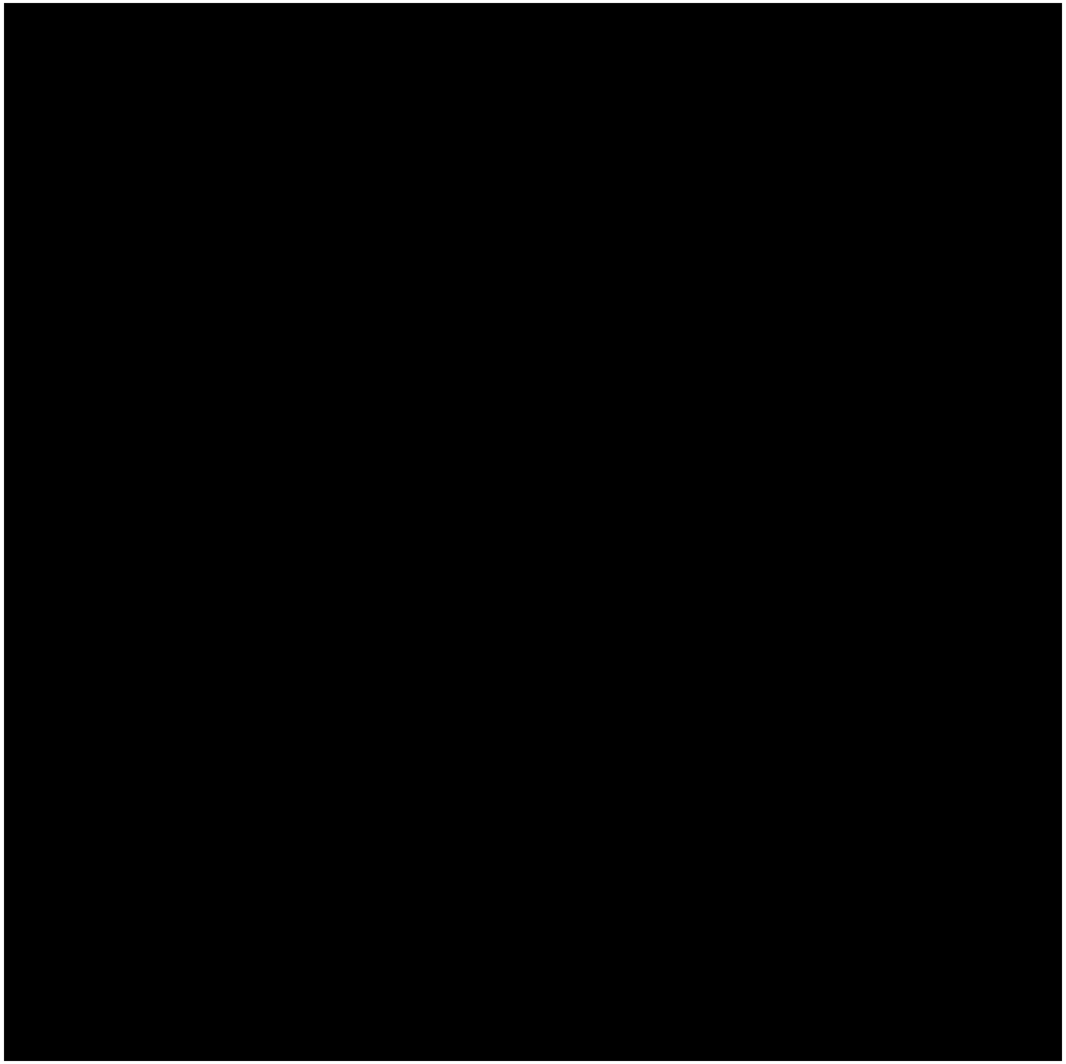


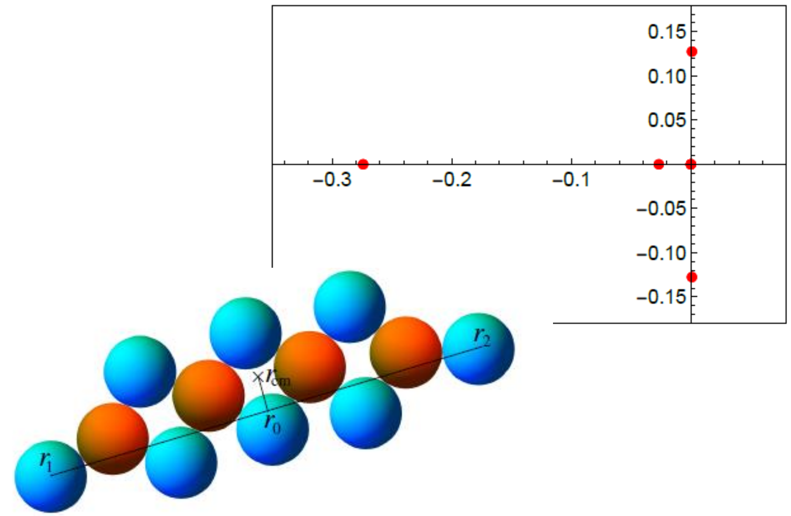
Inert molecules

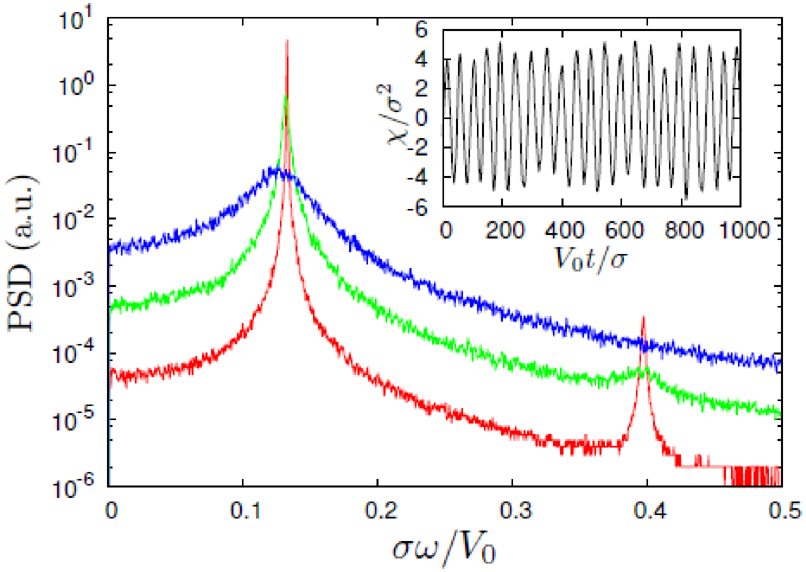


3D Structure determines **Function**, like proteins

Dynamic Function: Spontaneous Oscillation

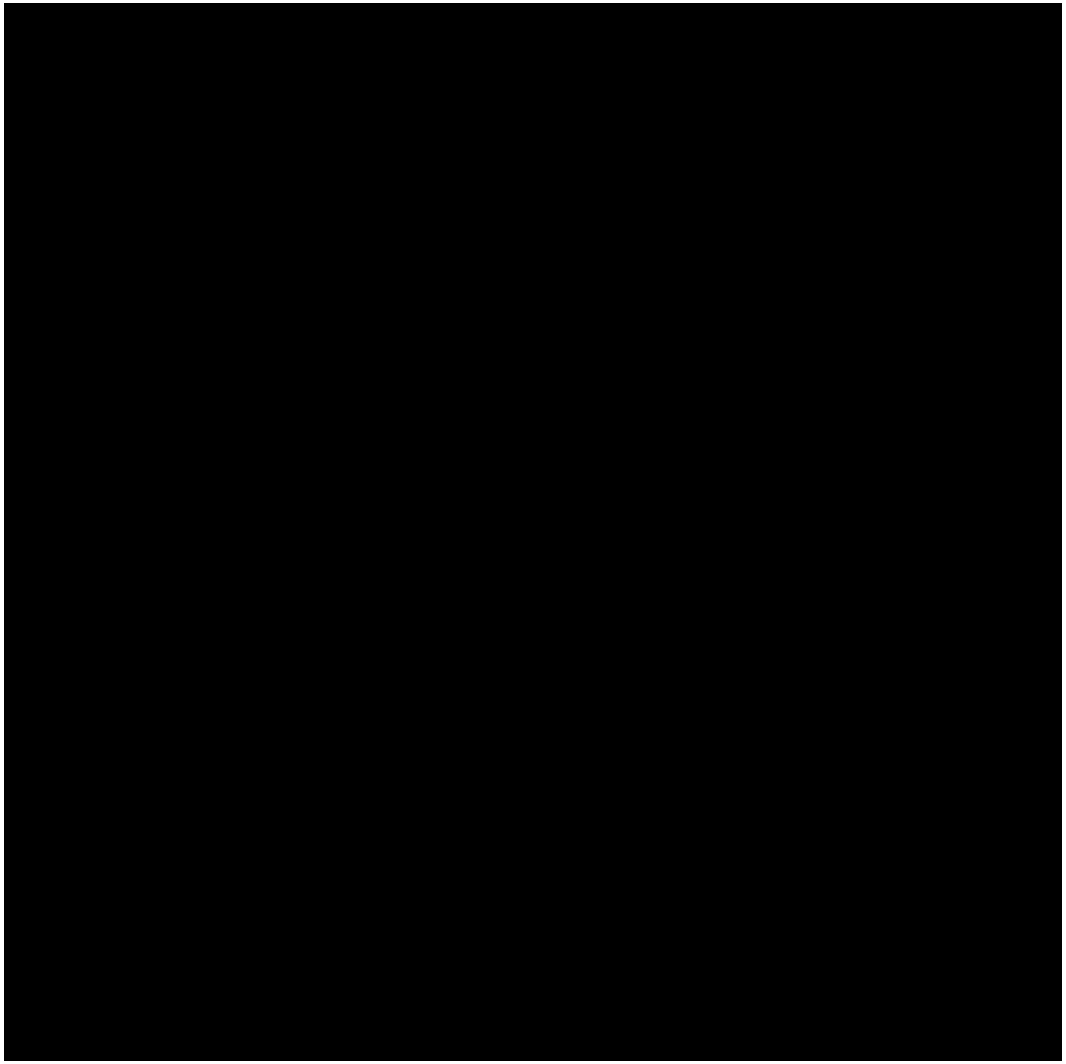


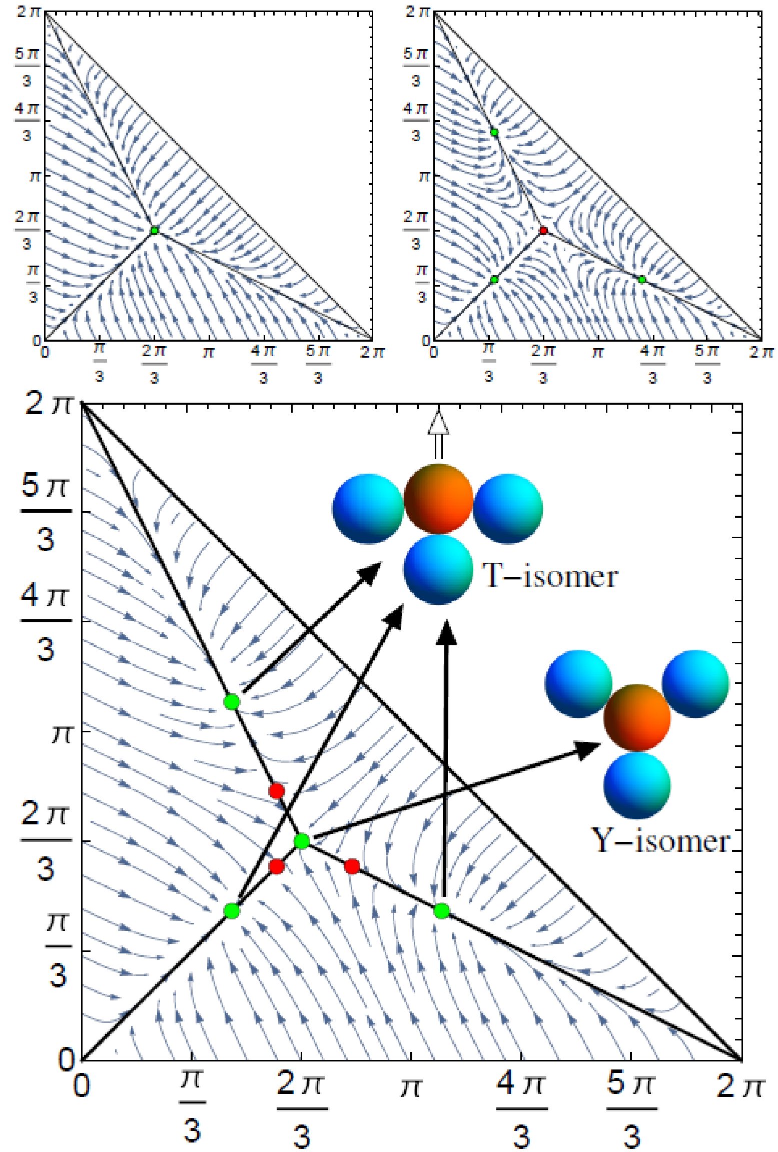




R. Soto & R. Golestanian (2015) arXiv:1502.07144

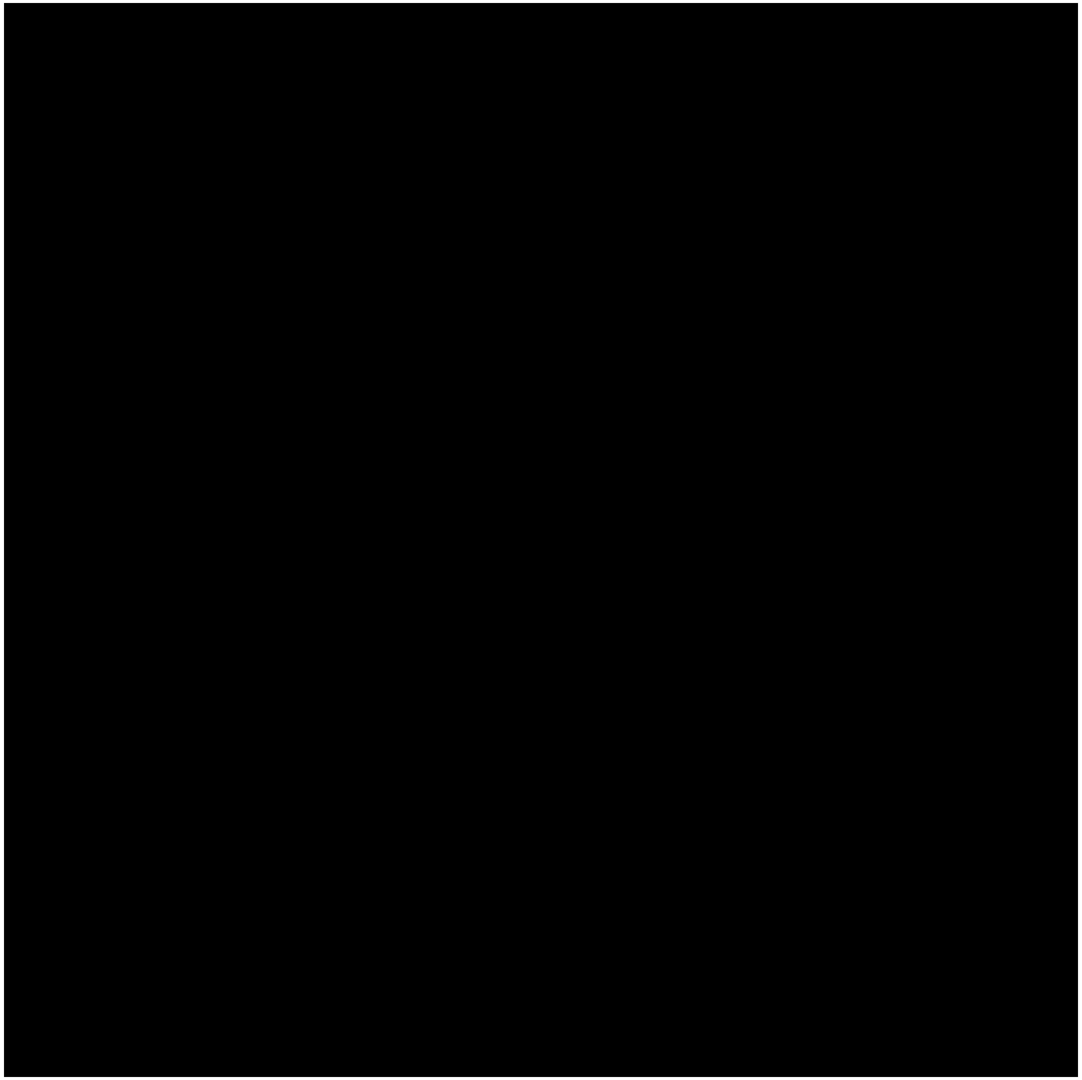
Dynamic Function: Run & Tumble





R. Soto & R. Golestanian (2015) arXiv:1502.07144

Dynamic Function: Beating & Swimming



self-assembled
“artificial sperm”

… and its history …

R. Soto & R. Golestanian (2015) arXiv:1502.07144

Part II

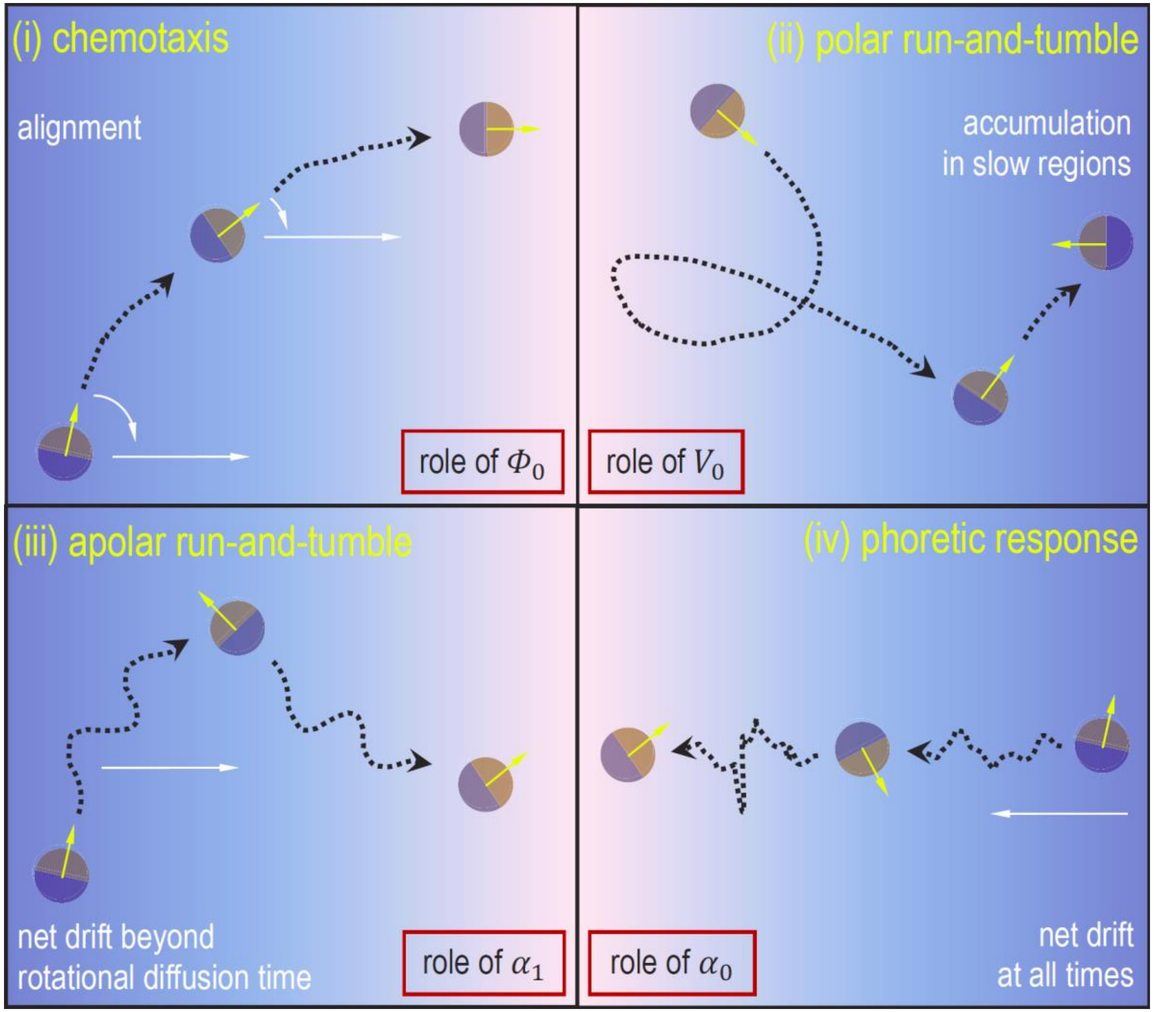
Chemical Activity

… Collective Chemotaxis of Janus Colloids…

Response to Nonuniform Chemical Profile

$$\mathrm{S} \to \mathrm{P}$$

$$\kappa(s) \equiv \kappa_2 \kappa_1 s / (\kappa_2 + \kappa_1 s)$$



Four Channels

with different origins

$$\boldsymbol{\omega} = \Phi_0(\sigma, \mu_p, \mu_s)\, \hat{\mathbf{n}} \times \boldsymbol{\nabla} s,$$

$$\mathbf{v} = V_0(s)\hat{\mathbf{n}} - \alpha_0 \boldsymbol{\nabla} s - \alpha_1 \hat{\mathbf{n}}\hat{\mathbf{n}} \cdot \boldsymbol{\nabla} s$$

S Saha, R Golestanian and S Ramaswamy (2014)

Parameters Give Design Rules

$$\Phi_0 = -\frac{3\mu_{s1}}{4R} - \frac{\kappa_1}{60D_p}\ (5\mu_{p1}\sigma_0 + 2\mu_{p2}\sigma_1 - \mu_{p1}\sigma_2)$$

$$V_0 = \frac{\kappa_1 s_b}{15D_p}(5\sigma_1\mu_{p0} + 2\sigma_2\mu_{p1} - \sigma_1\mu_{p2}),$$

$$\alpha_0 = -(\mu_{s0} + \frac{1}{10}\mu_{s2}) - \frac{\kappa_1 R}{10D_p}(\sigma_0\mu_{p2} - \frac{2}{9}\sigma_1\mu_{p1} - 2\sigma_2\mu_{p0} + \frac{1}{35}\sigma_2\mu_{p2}),$$

$$\alpha_1 = -\frac{1}{10}\mu_{s2} - \frac{\kappa_1 R}{30D_p}(10\sigma_0\mu_{p0} + \sigma_0\mu_{p2} + 2\sigma_1\mu_{p1} - 2\sigma_2\mu_{p0} + \frac{29}{35}\sigma_2\mu_{p2}).$$

$$\Omega_0 = -\frac{3\mu_{p1}}{4R},\quad \beta_0 = -(\mu_{p0} + \frac{1}{10}\mu_{p2}),\quad \beta_1 = -\frac{1}{10}\mu_{p2}$$

Many-Colloid Theory

$$
\begin{aligned}
\frac{\mathrm{d}\mathbf{r}_\alpha}{\mathrm{d}t} &= V_0(s)\hat{\mathbf{n}}_\alpha - \alpha_0\nabla s - \alpha_1\hat{\mathbf{n}}_\alpha\hat{\mathbf{n}}_\alpha\cdot\nabla s + \beta_0\nabla p \\
&\quad +\beta_1\hat{\mathbf{n}}_\alpha\hat{\mathbf{n}}_\alpha\cdot\nabla p + \sqrt{2D}\,\mathbf{f}^r_\alpha(t), \\
\frac{\mathrm{d}\mathbf{n}_\alpha}{\mathrm{d}t} &= \Phi_0(\hat{\mathbf{n}}_\alpha\times\nabla s)\times\hat{\mathbf{n}}_\alpha + \Omega_0(\hat{\mathbf{n}}_\alpha\times\nabla p)\times\hat{\mathbf{n}}_\alpha \\
&\quad +\sqrt{2D_r}\,\hat{\mathbf{n}}_\alpha\times\mathbf{f}^n_\alpha(t),
\end{aligned}
$$

From coupled Langevin equations to a hierarchy of equations for the density field, the polarisation field, etc

with all the coefficients known

in terms of the microscopic parameters

that can be tuned by changing the surface chemistry and geometry.

Collective Behaviour

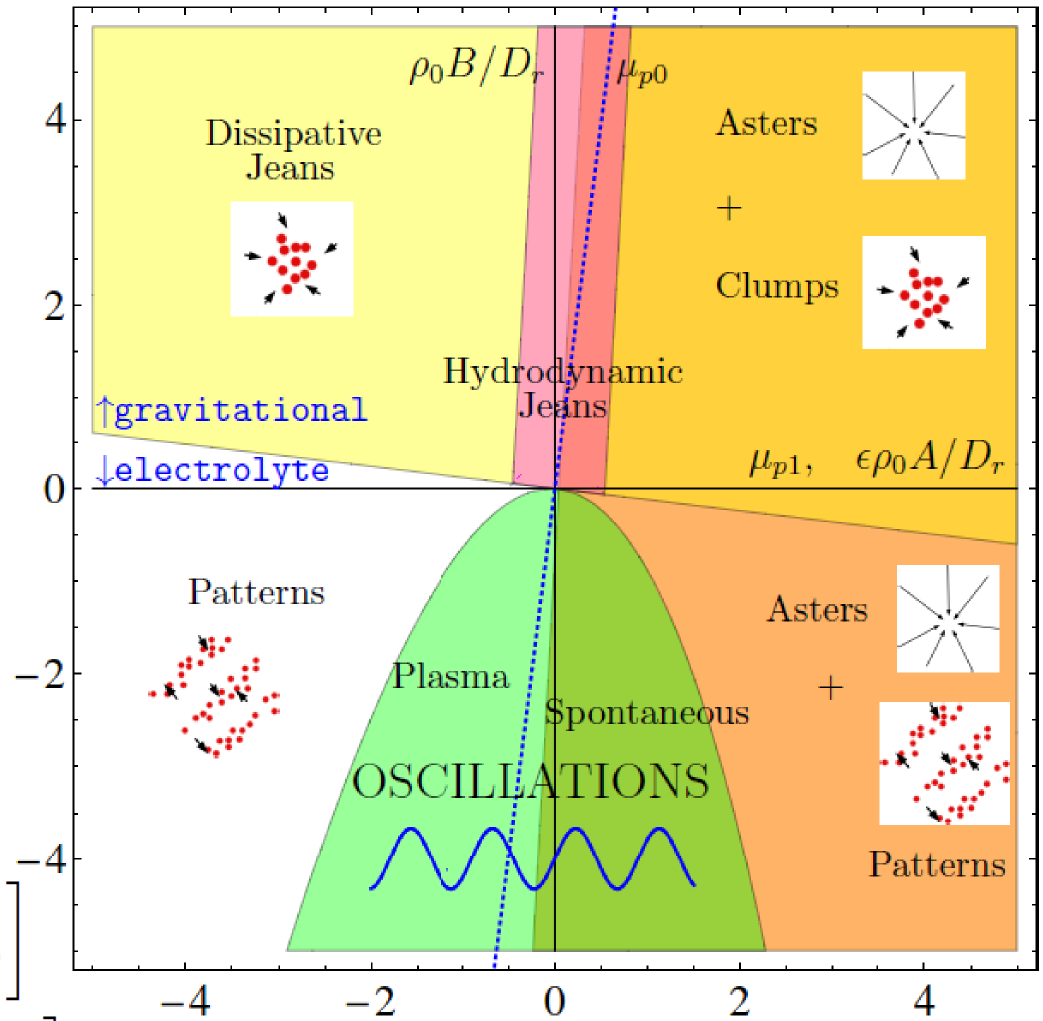
Interplay between self-propulsion, spin, drift, alignment, driven by and mediated via chemicals

-> Variety of Behaviours:

- Clustering
- Aster condensation
- Pattern formation
- Plasma Oscillations
- Ringing

$$A = N\kappa(s_0)\left[\frac{\Omega_0}{D_p} - \frac{\Phi_0}{D_s} + \frac{V_0(s_0)}{2D_s}\frac{d\ln\kappa}{ds}|_{s_0}\right]$$

$$B = N\kappa(s_0)\left[\frac{1}{D_p}(\beta_0 + \frac{\beta_1}{3}) + \frac{1}{D_s}(\alpha_0 + \frac{\alpha_1}{3})\right]$$



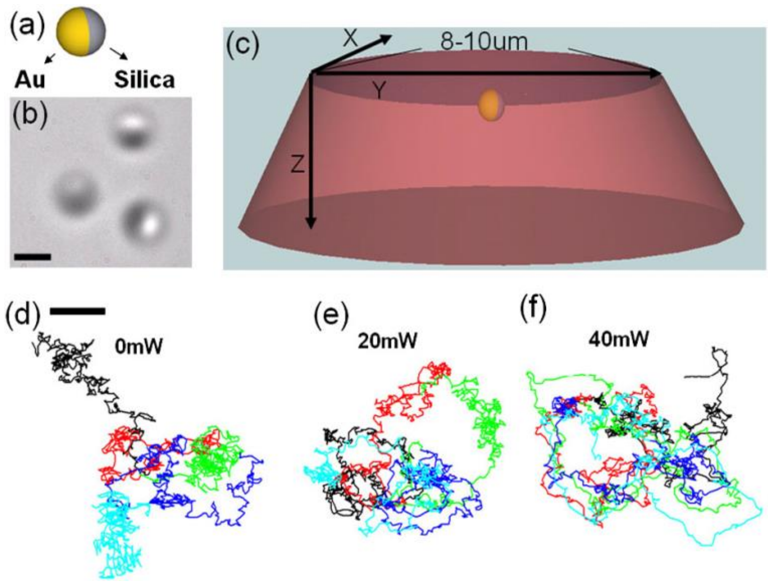
<u>Part III</u>

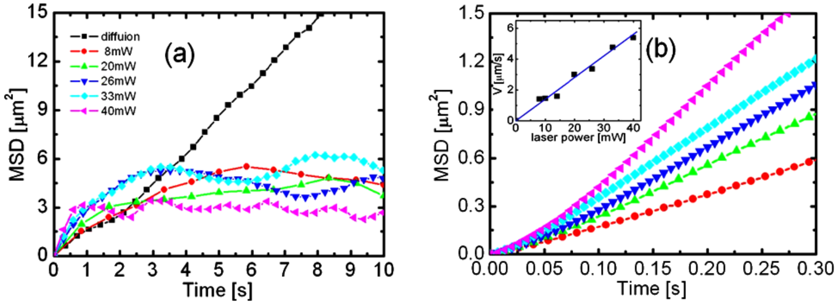
Thermal Activity

… self-organised phototactic swarms …

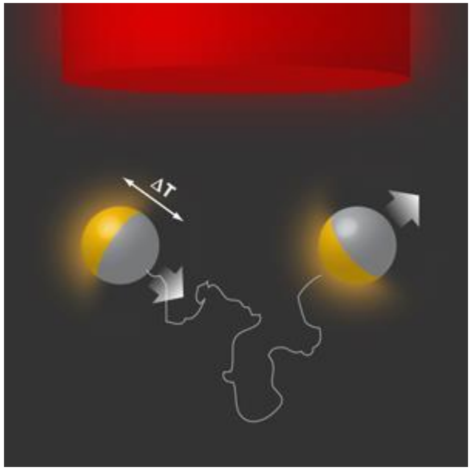
Self-Thermophoresis

Experiment





Mechanism



R. Golestanian, T.B. Liverpool & A. Ajdari (2007)

H-R. Jiang, N. Yoshinaga & M. Sano, PRL **105**, 268302 (2010)

Collective Thermotaxis

- Intra-colloid Activity
  - Mobile heat source
  - Self-propelled, if asymmetric

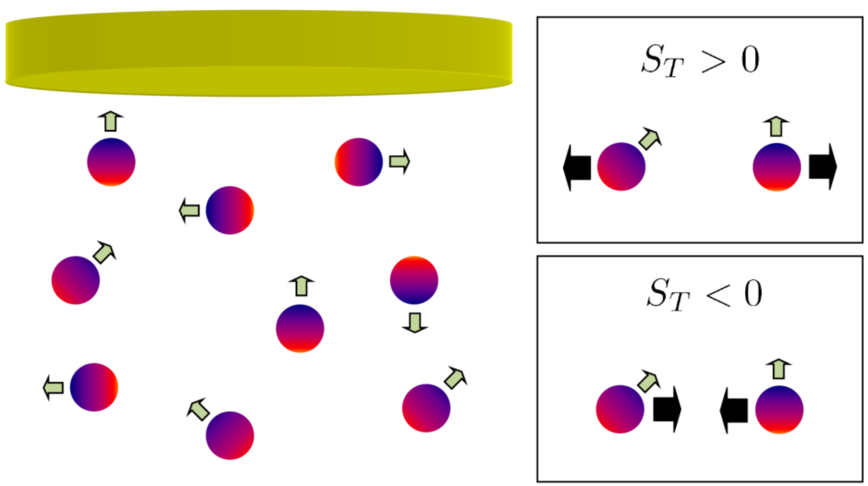
$$v_0 = \frac{\epsilon I D_T}{6\kappa}$$

- Inter-colloid Interaction

$$\mathbf{v} = -D_T \nabla T$$

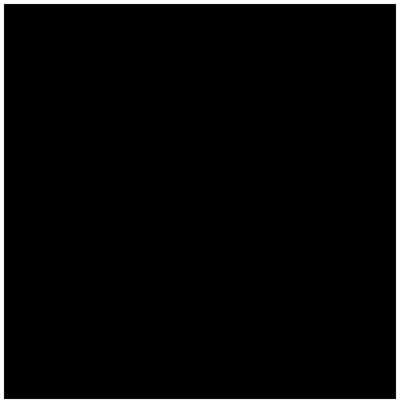
  - Thermo-repulsive
  - Thermo-attractive

$$S_T = \frac{D_T}{D}$$

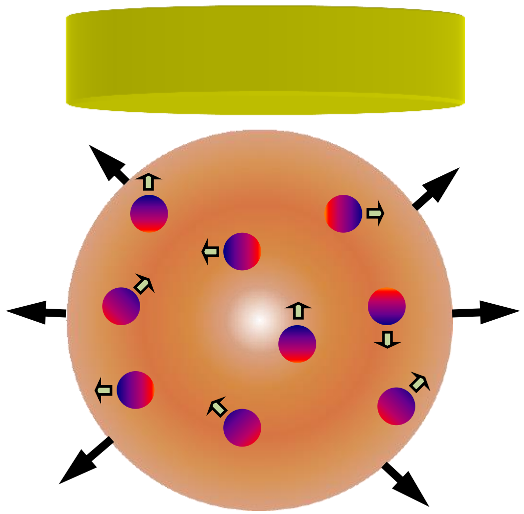


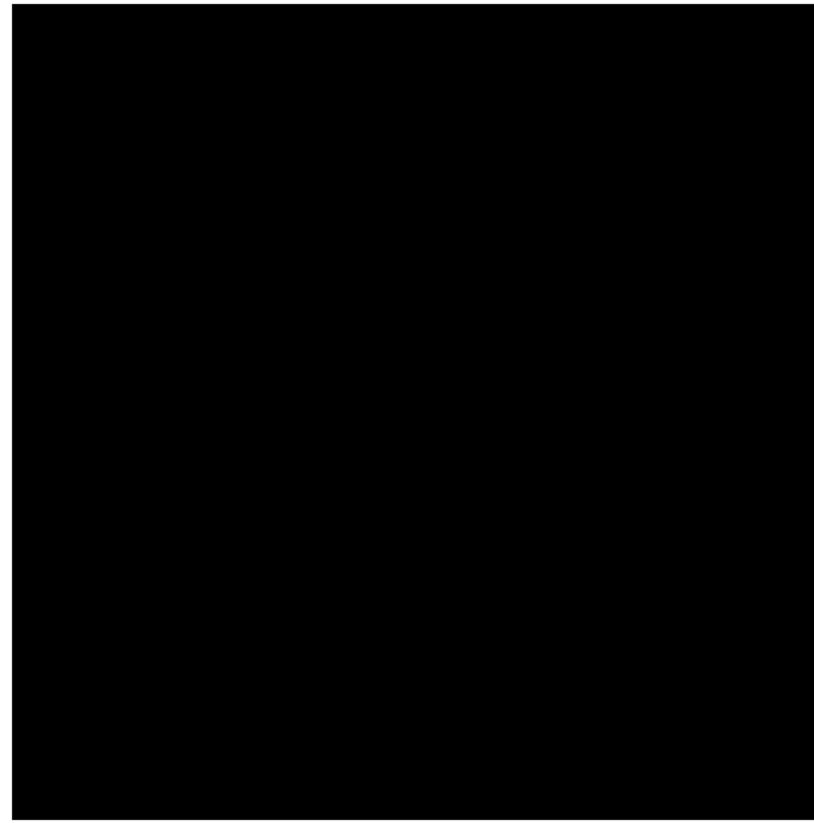
R. Golestanian (2012)

Thermo-Attractive (“Gravitational”) Case



colloidal “star”



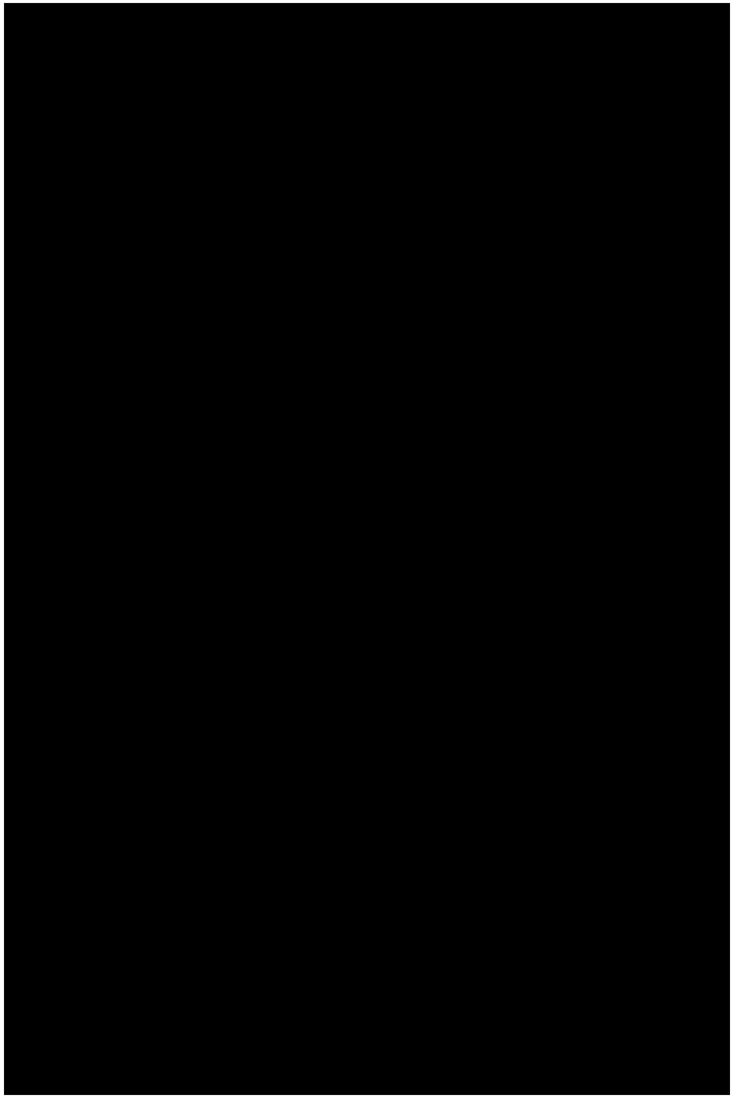


colloidal “supernova”

- Heat flux at the boundary cannot balance the heat generated inside -> uncontrolled build-up of heat
- In molecular systems: exothermic combustion reactions -> thermal explosion!

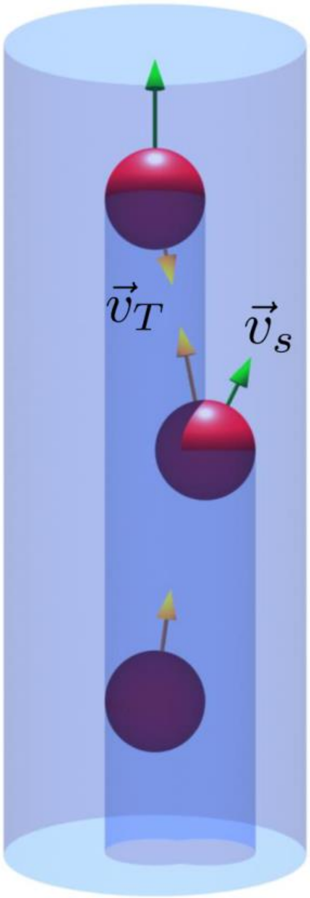
D.A. Frank-Kamenetskii, “Calculation of thermal explosion limits.” Acta. Phys. Chin., URSS **10**, 365-370 (1939)

Collective Phototaxis



- Thermophoresis
- Attraction
- Excluded volume
- Shadowing

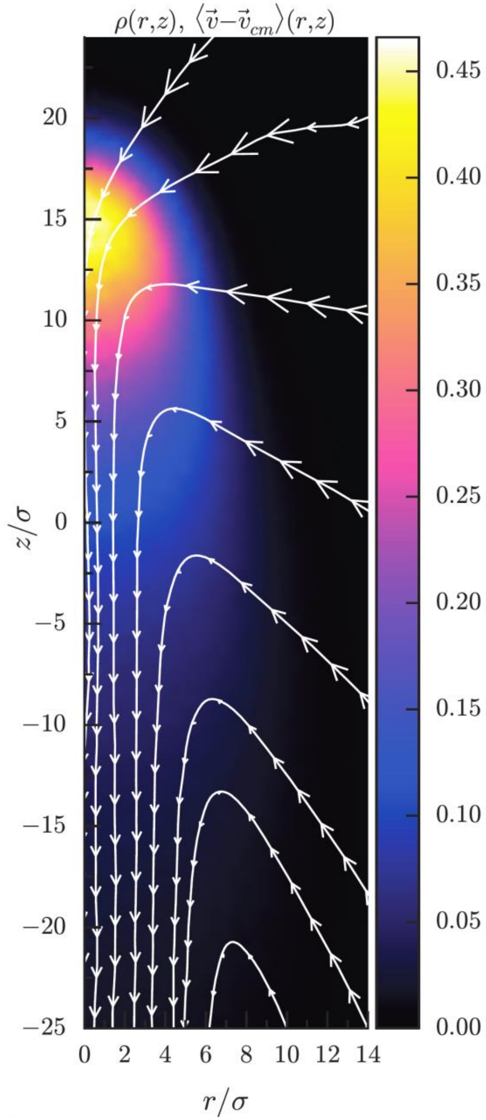
- uniform illumination from the top
- propulsion due to self-generated gradT
- mutual attraction due to gradT caused by mobile heat sources

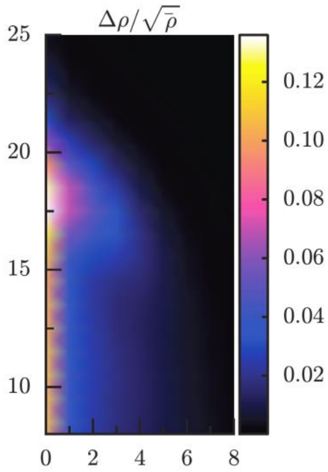


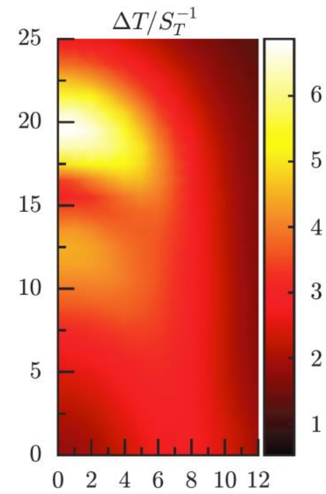
J.A. Cohen & R. Golestanian (2014)

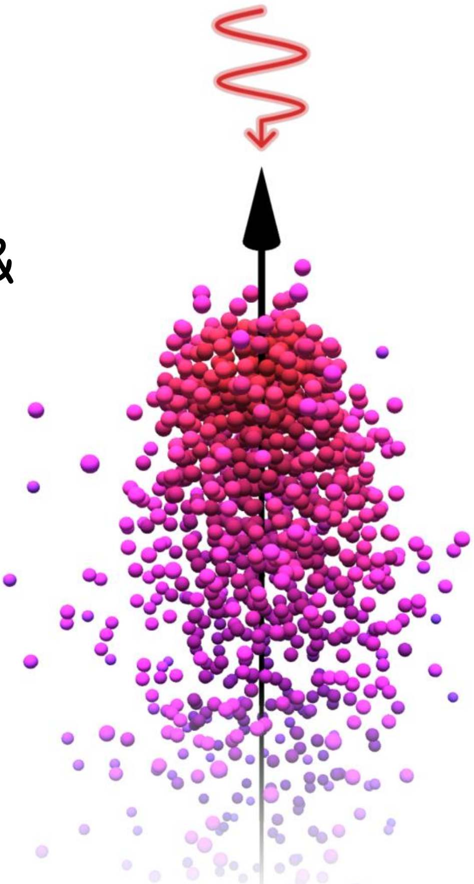
Comet-like Swarming

- uniform average motion
- hot-and-dense head
- circulation
- large density fluctuations & temperature fluctuations







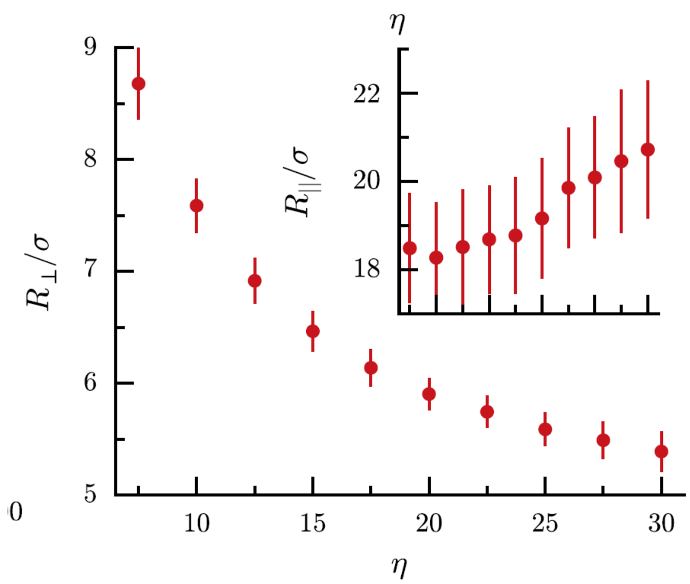


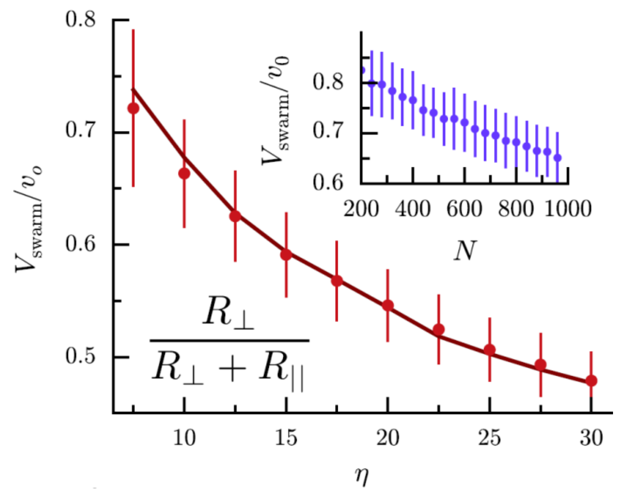
Changing the Coupling Strength

$$\eta = \sigma \epsilon I |S_T| / \kappa$$

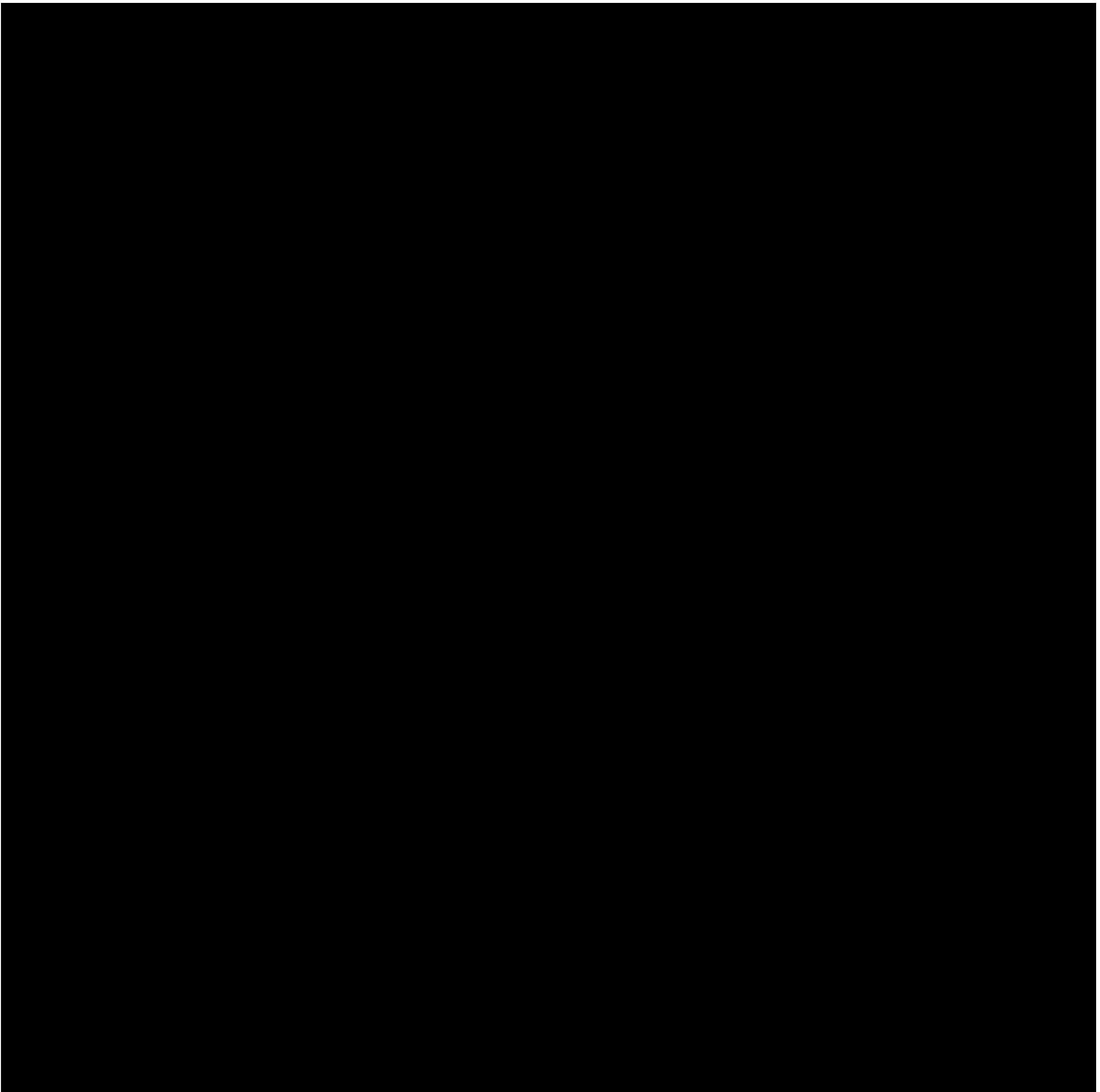
As the coupling strength increases, the Swarm:

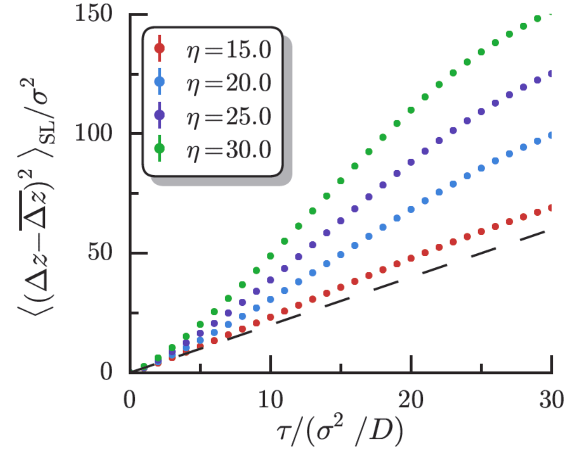
- elongates
- narrows down
- slows down
- becomes more dynamic

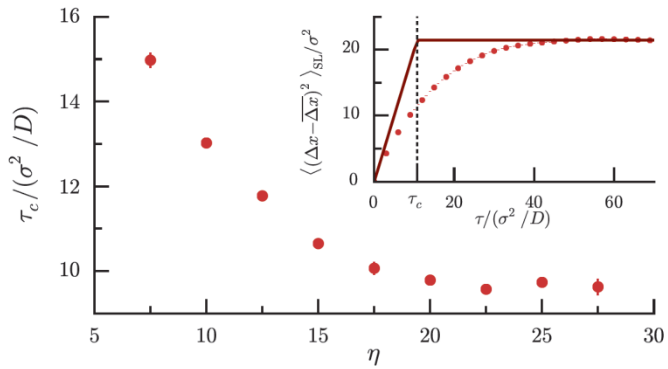




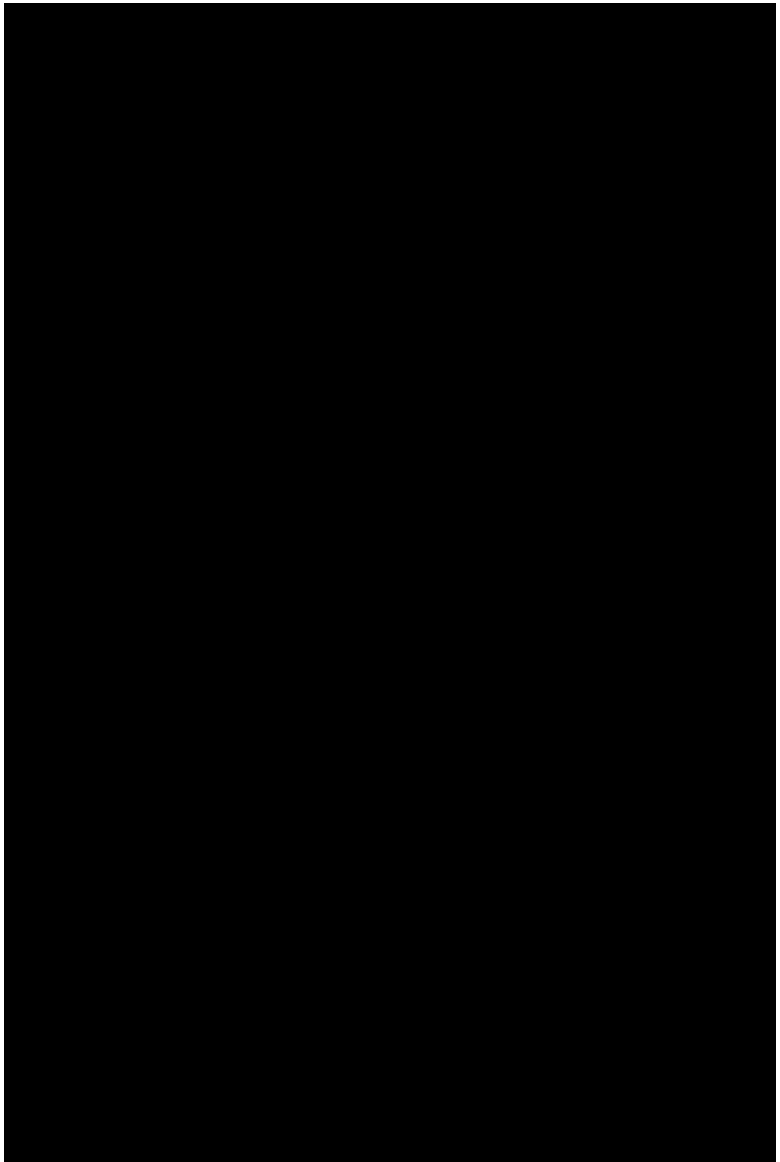
Particle Tracking: Super-diffusion & Confinement

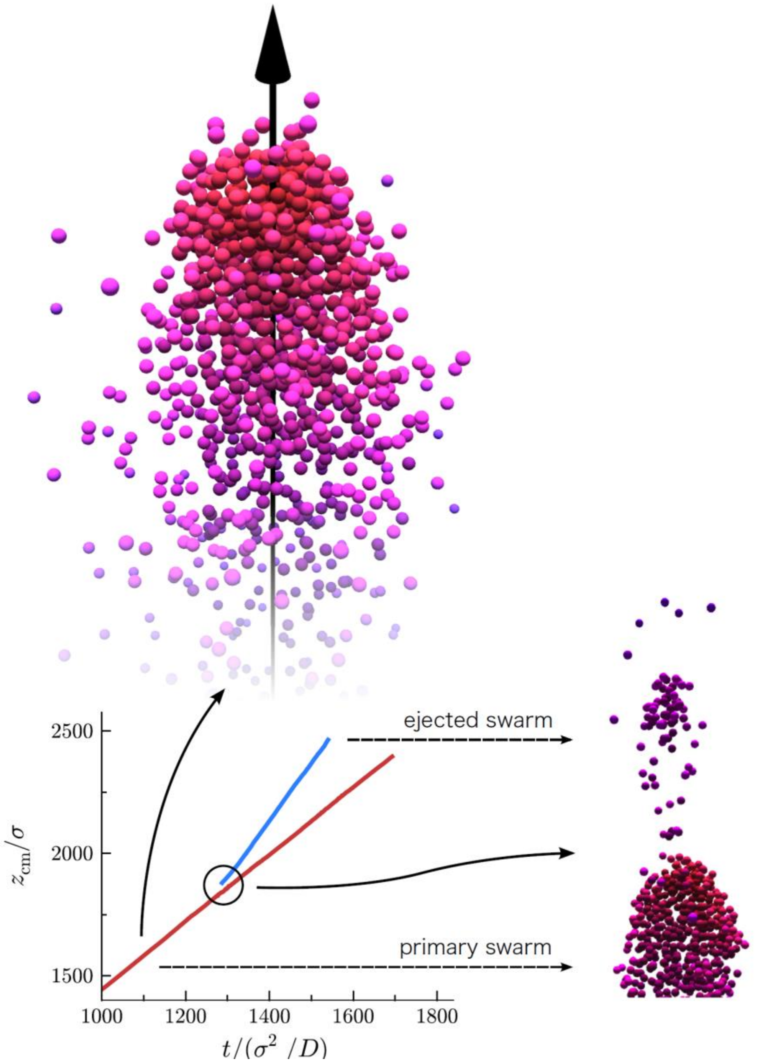




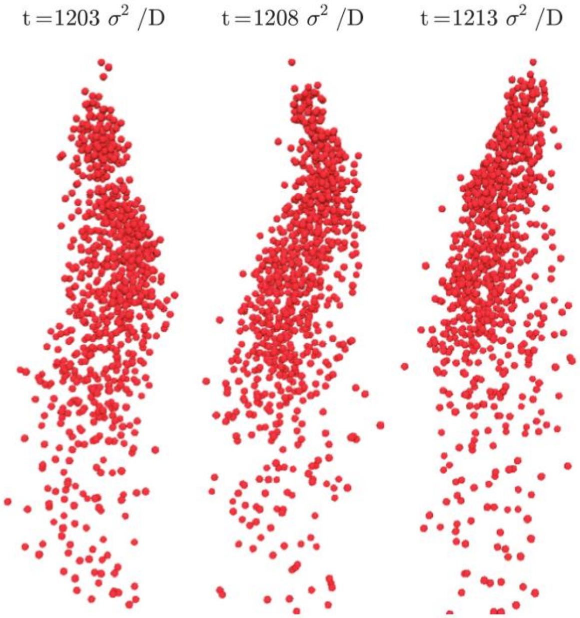


Increased Coupling Behaviour: Fission

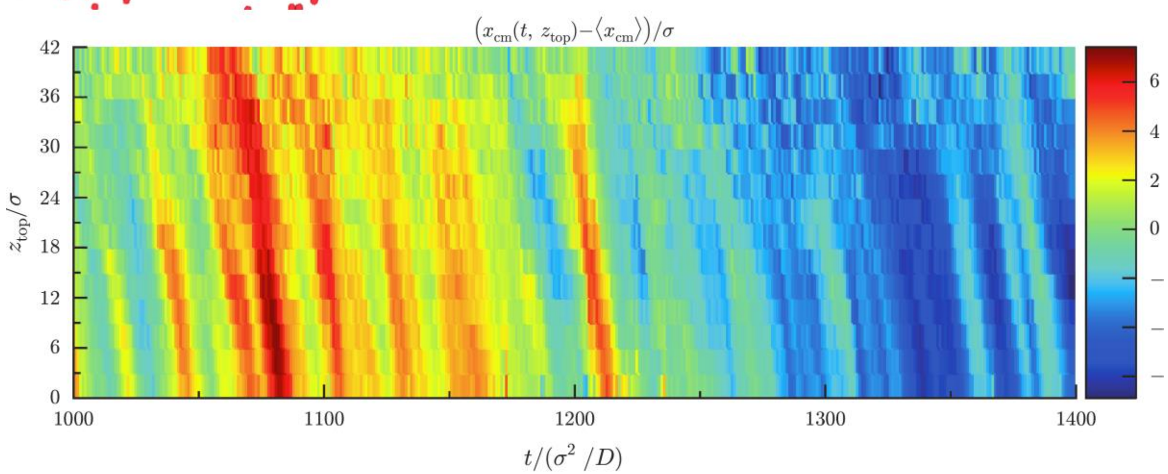




Increased Coupling Behaviour: Waves



- waves can start randomly
- they propagate from tail to head
- constant propagation velocity
- no dispersion or damping



Conclusion

Collective behaviour of active colloids could be very rich due to the long-range nature of their **chemical** or **thermal** interactions.