Self-organization & Collective Behaviour of Active Colloids

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Active Matter: Cytoskeleton, Cells, Tissues and Flocks
KITP, UCSB
March 21, 2014

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?



Ebbens et al, PRE **82,** 015304 (R) (2010)

Non-equilibrium Transport: Phoretic Motion

- Electrophoresis

  Smoluchowski (1903)

- Thermophoresis

  Ludwig (1856), Soret (1879)

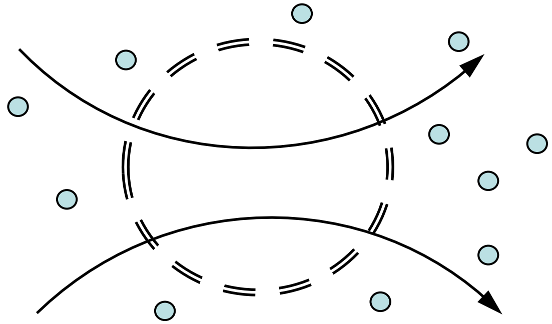
- Osmophoresis

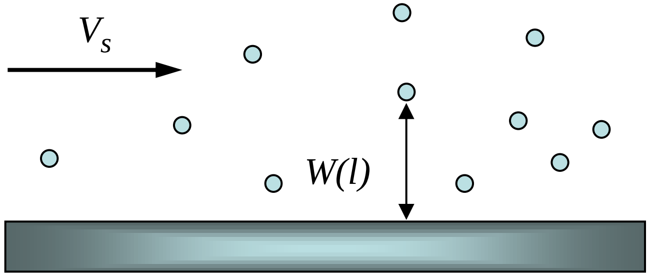
  Sackmann *et al* (1999)

- Diffusiophoresis

  Derjaguin *et al* (1961),

  Anderson & Prieve (1984)

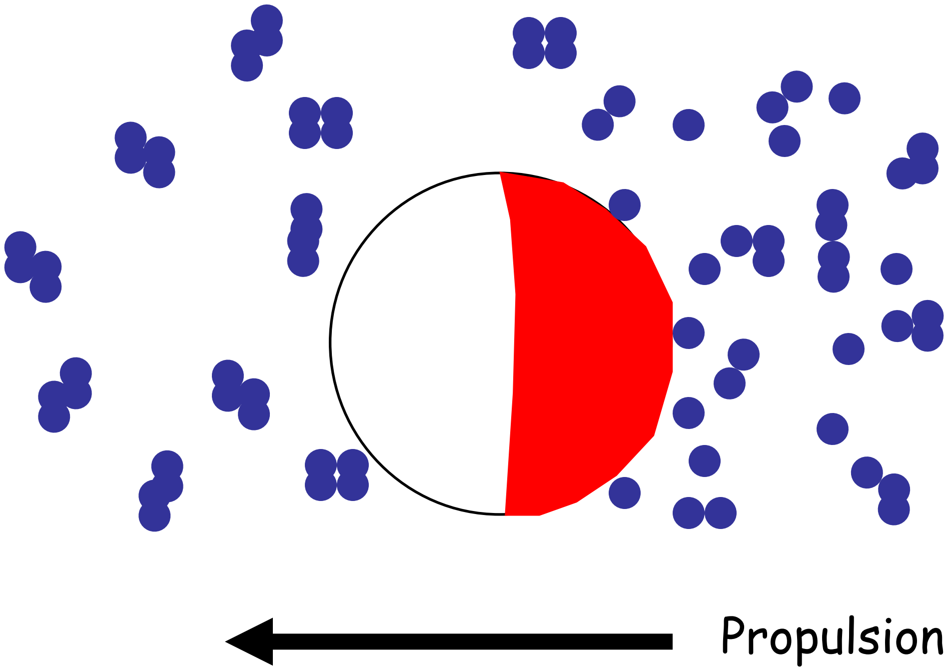




Phoretic Transport is Force-Free

Propulsion via Self-Phoresis

e.g. self-diffusiophoresis



Chemical reaction produces more products than reactants

Propulsion (repulsive interaction)

Particle half-coated with catalyst

Golestanian, Liverpool & Ajdari (2005)

Analysis of the Motion

- Slip Velocity

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

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

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

mobility

- Source at the Surface

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

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

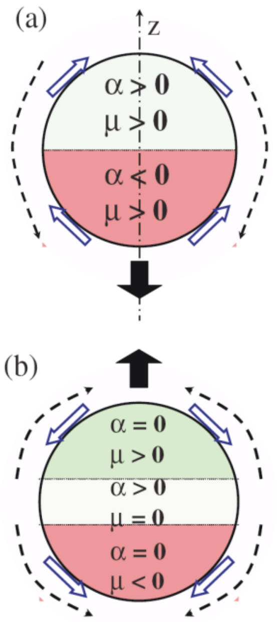
activity

Propulsion via Self-Phoresis

- Swimming Velocity

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

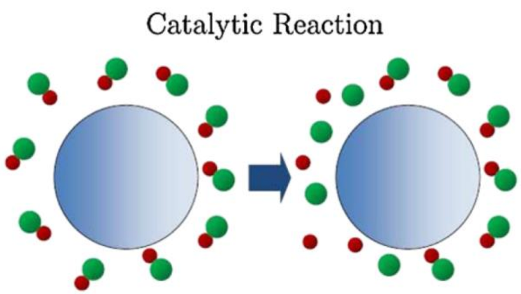
- Design-related Questions
  - Symmetry breaking
  - Relative importance of activity/mobility
  - Effect of Geometry

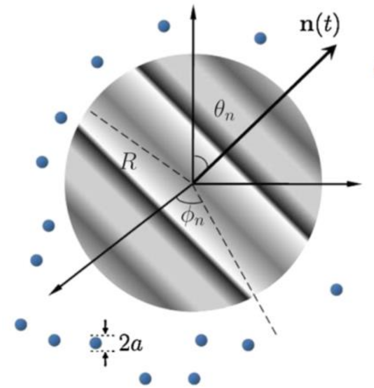


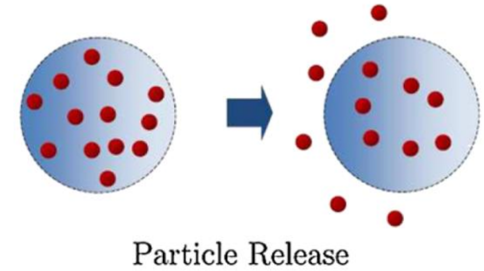
- Generic for Any Phoresis

  -> Self-Thermophoresis

Stochastic Dynamics of Phoretic Swimmers





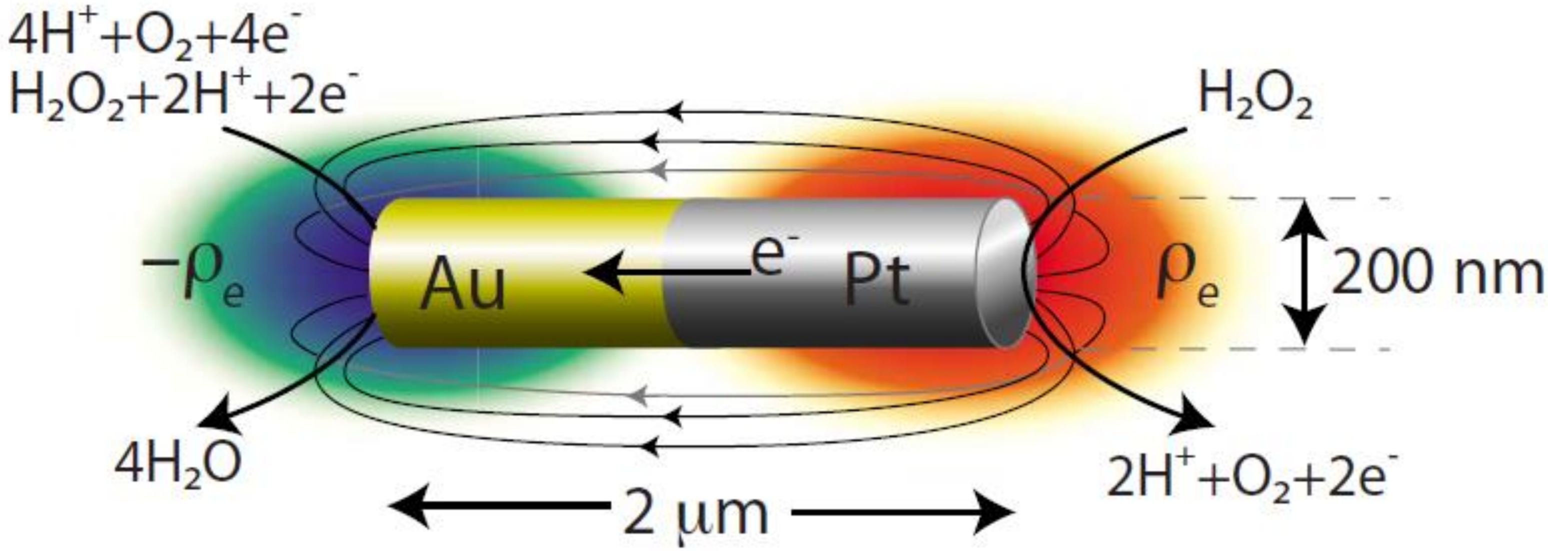


Asymmetric Contribution	$\sim t^2$ *inertial*	$\sim t^2$ *propulsive*	$\sim t^2 - \gamma\, t^{3/2}$ *propulsive + anomalous*	$\sim t$ *diffusive*
Symmetric Contribution	$\sim t^2$ *inertial*	$\sim t^{3/2}$ *anomalous*	$\sim t$ *diffusive*	
Hydrodynamic Contribution	$\sim t^2$ *inertial*	$\sim t - \beta\,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

τ_h τ_d τ_r

Golestanian (2009)

Experiments on Self-Phoresis

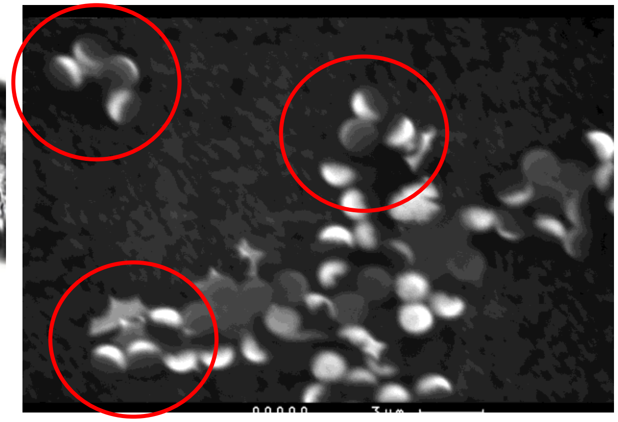


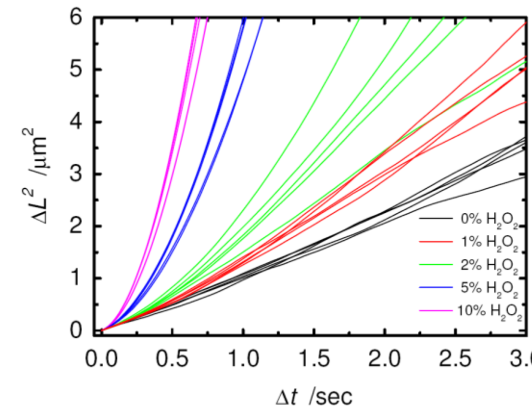
Paxton et al, JACS **126**, 13424 (2004) [Ayusman Sen Group]

Redox Self-Electrophoresis: a short circuited battery!

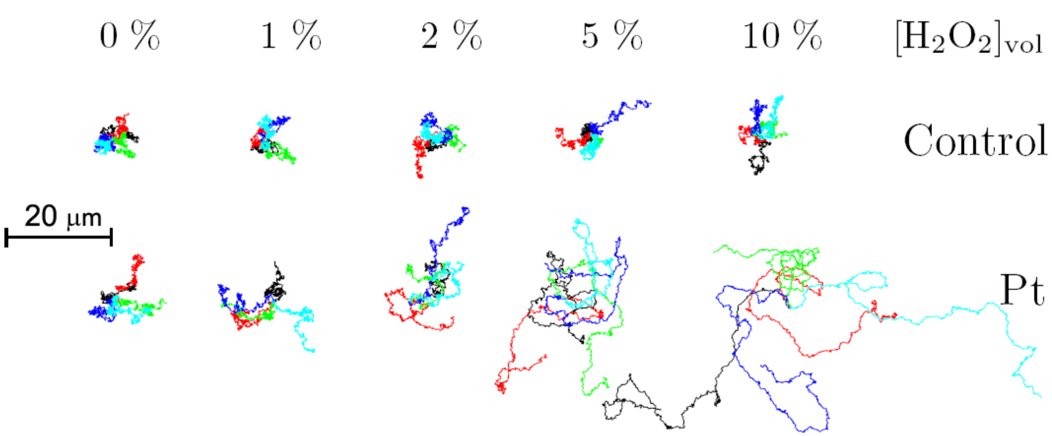
Theoretical Analysis: Moran, Wheat & Posner, PRE **81,** 065302(R) (2010)

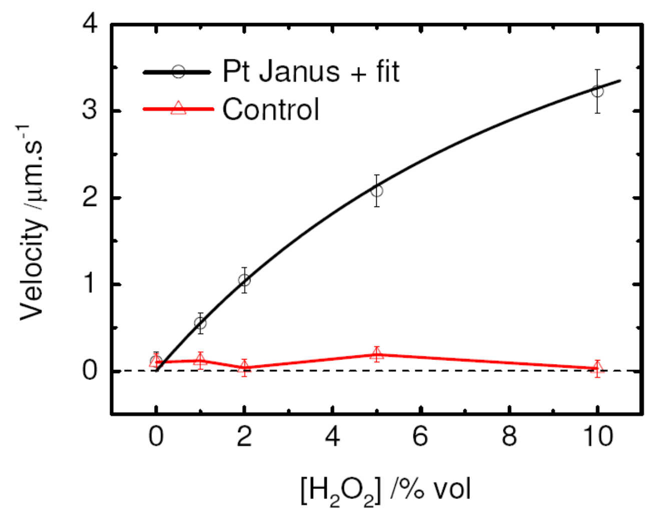
Experiments on Self-Phoresis





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

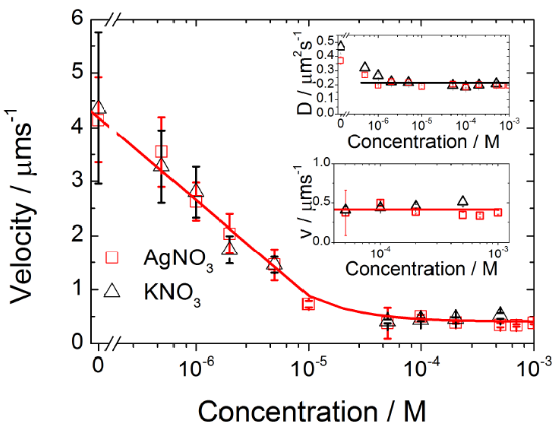


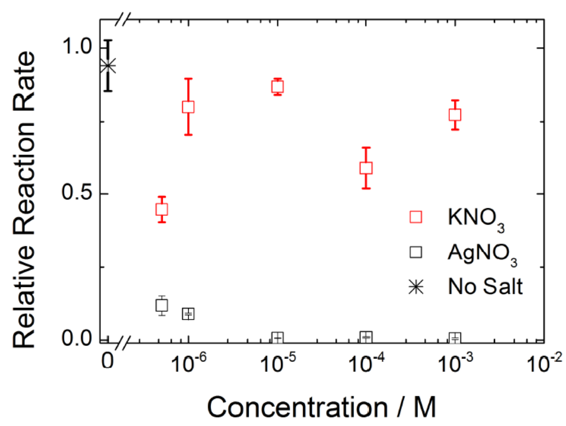


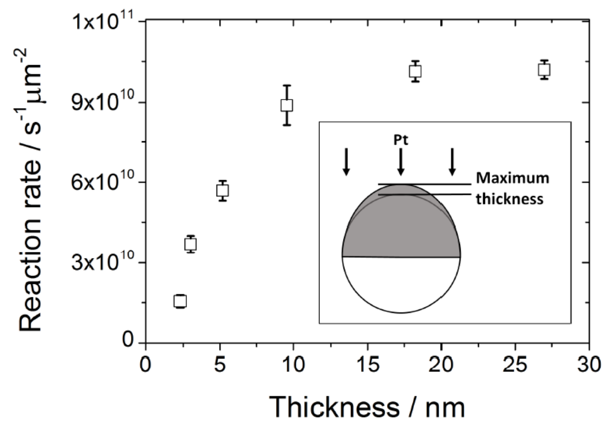
Howse et al, PRL **99,** 048102 (2007)

Experiments on Self-Phoresis

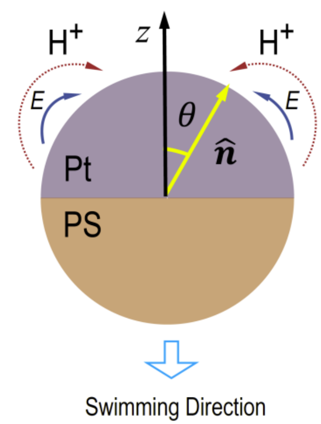
There are subtle electrokinetic effects for the Pt-PS beads …

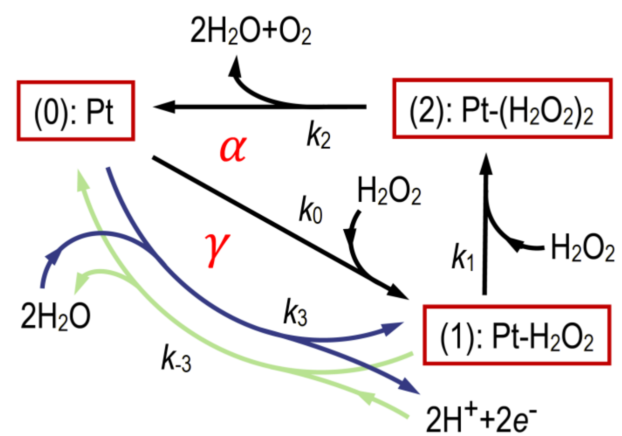






- nested loops
- charged intermediates

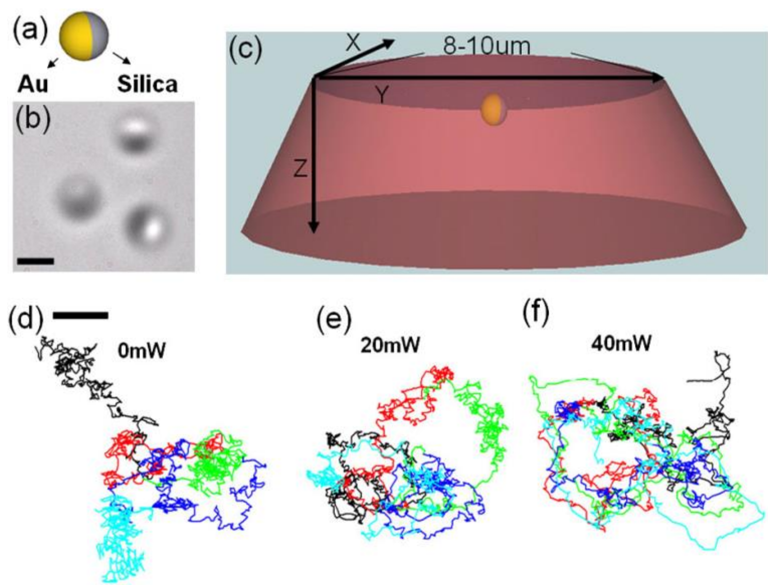


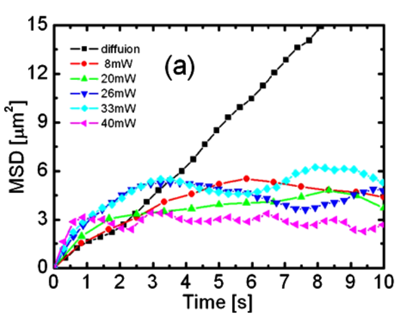


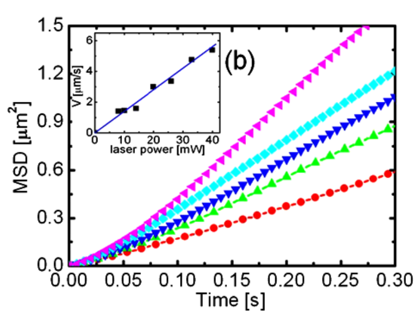
- S. Ebbens, D.A. Gregory, G. Dunderdale, J.R. Howse, Y. Ibrahim, T.B. Liverpool & R. Golestanian, arXiv:1312.6250
- A. Brown & W. Poon, arXiv:1312.4130

Experiments on Self-Phoresis

Self-Thermophoresis

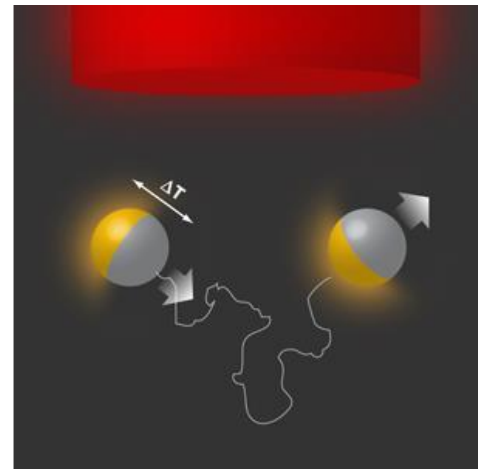






Jiang, Yoshinaga & Sano, PRL **105**, 268302 (2010)

The Mechanism



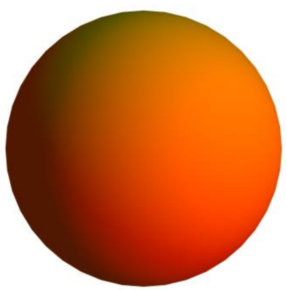
Golestanian, Liverpool & Ajdari (2007)

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!
(as in relationships, 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

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

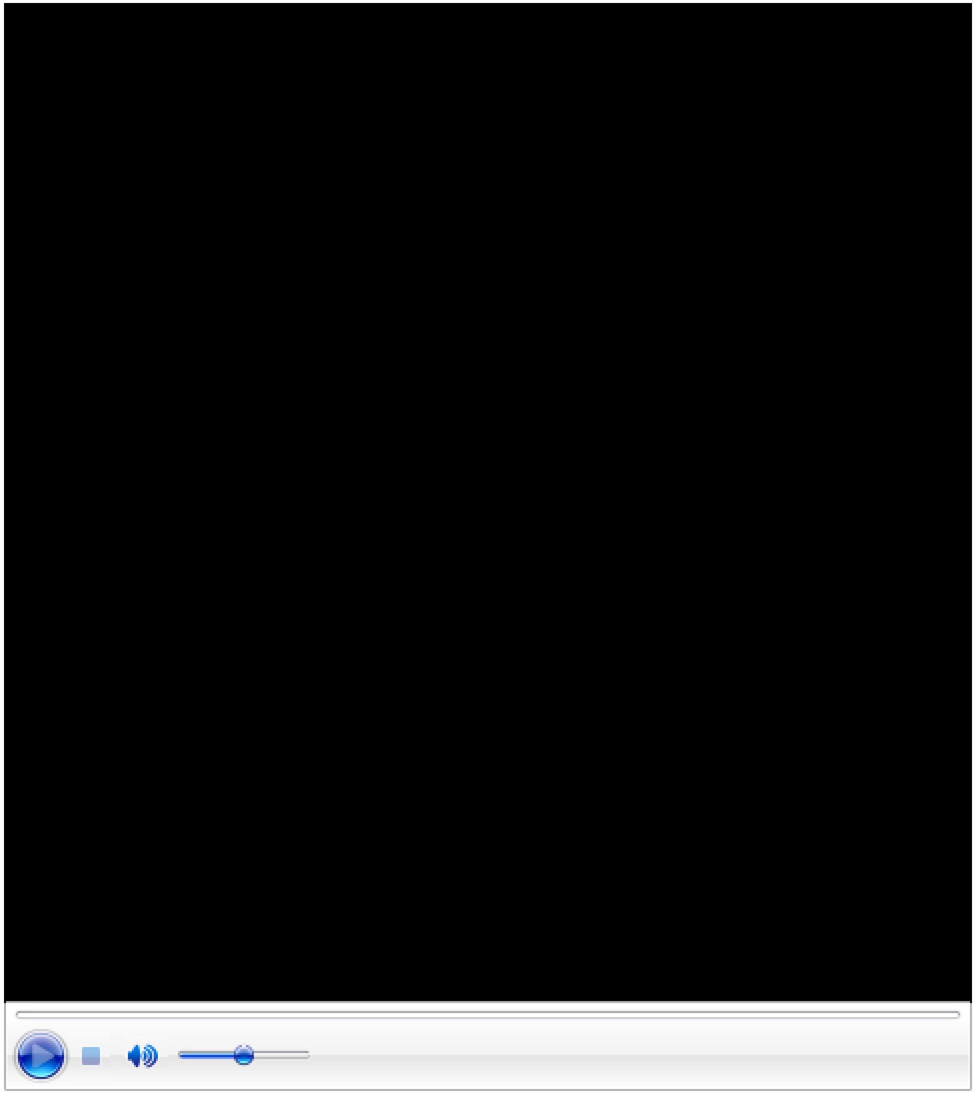
B  $\widetilde{\alpha}_B = \widetilde{\mu}_B = -1$

AB, AB_2, AB_3, ... , AB_n

A

$\widetilde{\alpha}_A = 3$

$\widetilde{\mu}_A = 0$



B

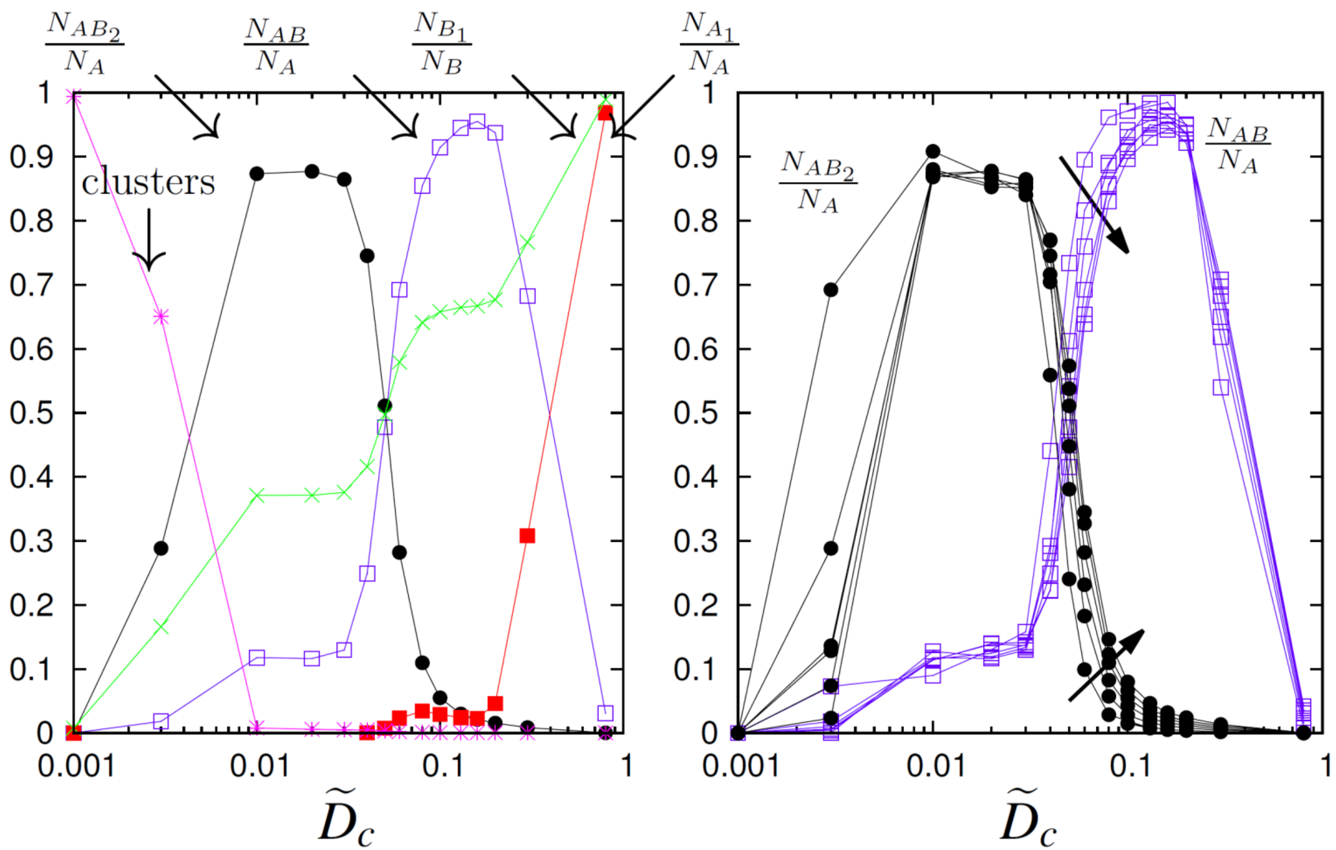
$\widetilde{\alpha}_B = \widetilde{\mu}_B = -1$

Molecular Populations vs Temperature

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

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

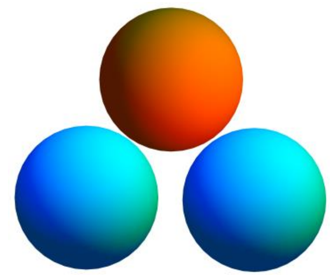
Stable molecules are not necessarily "charge neutral"



AB$_2$ Isomers

linear

Inert



planar

Self-propelled

preferred angle 180 deg

preferred angle 60 deg

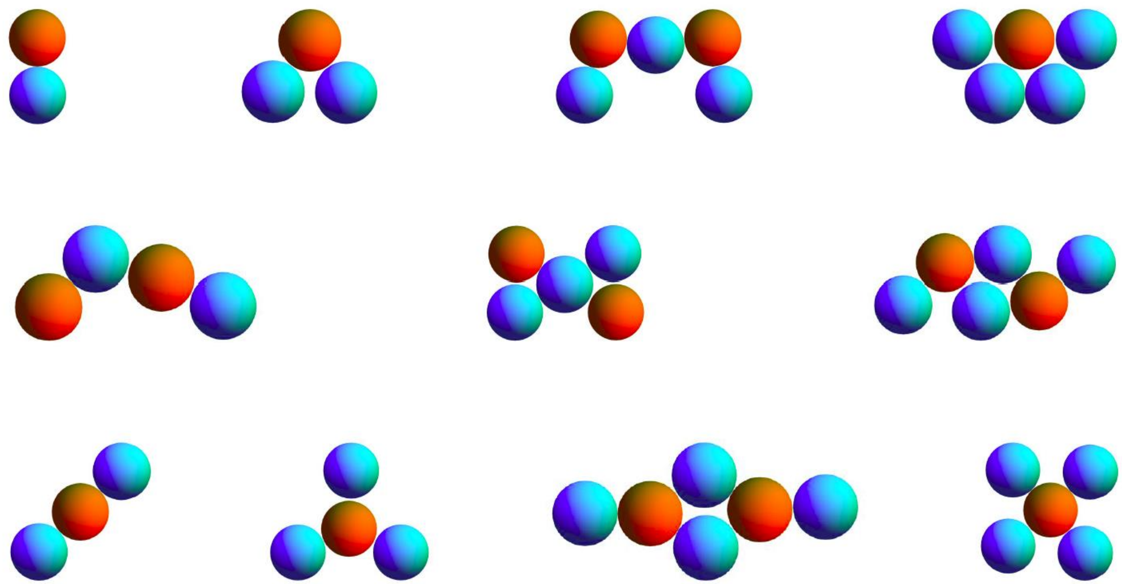
We observe isomerization and bi-stability

Tabulating Active Molecules

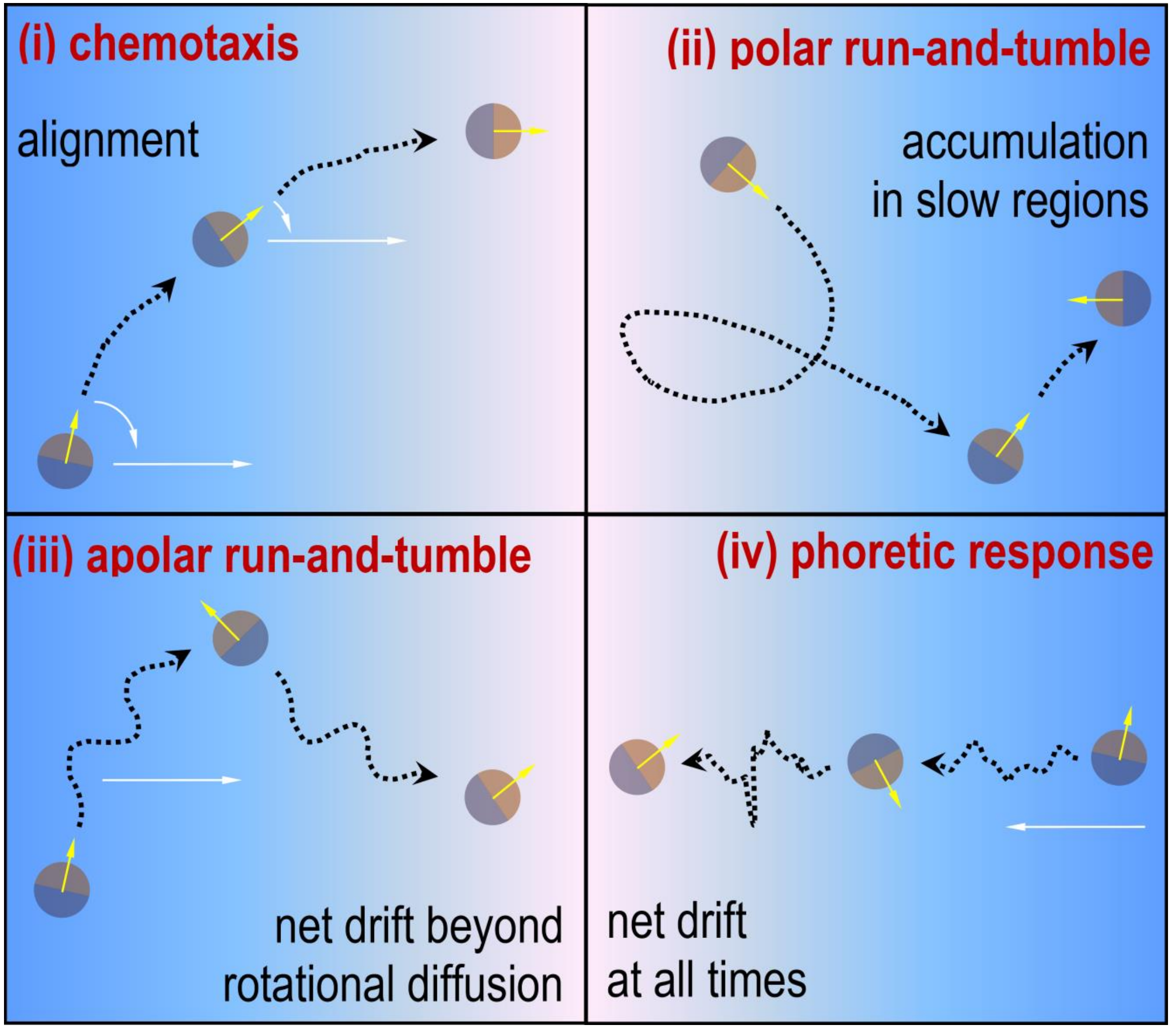
Translational propulsion

Rotational propulsion

Inert molecules



Response to Nonuniform Chemical Profile



Saha, Golestanian & Ramaswamy (2014)

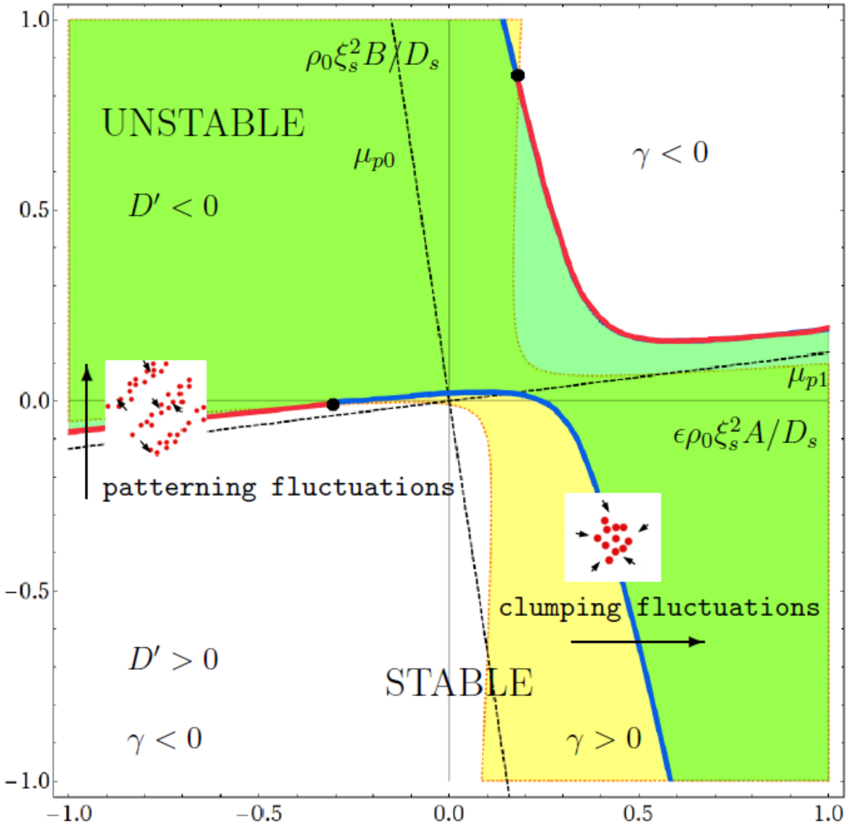
Many-Colloid Chemotaxis: Screened Case

Michaelis-Menten rule
leads to screening

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

Screening length:

$$\xi_s = [N \rho_0 \kappa'(s_0)/D_s]^{-1/2}$$



Signature in density field:
Instabilities and Fluctuations

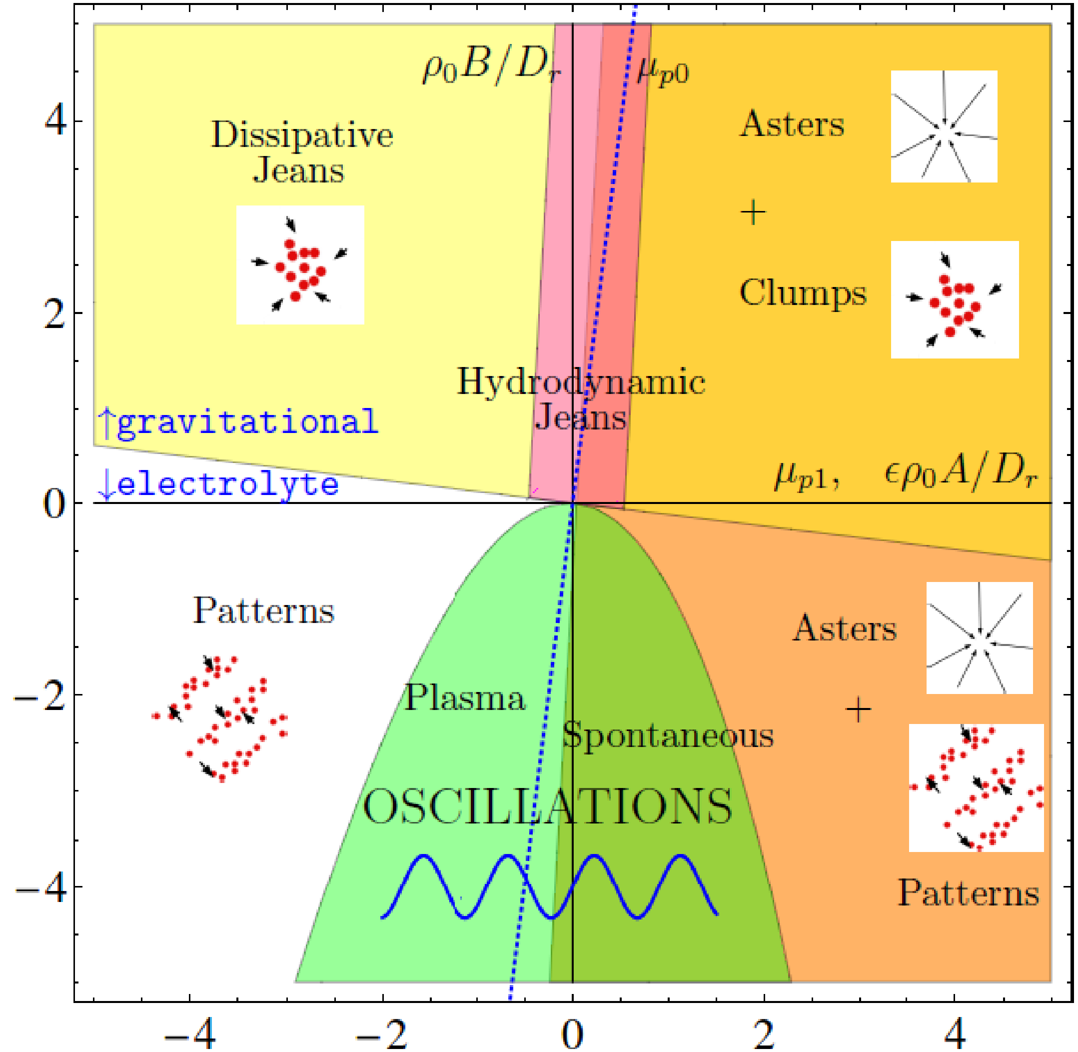
No flocking.

Collective Behaviour: Unscreened Case

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

-> Variety of Behaviours:

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



Collective Thermotaxis

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

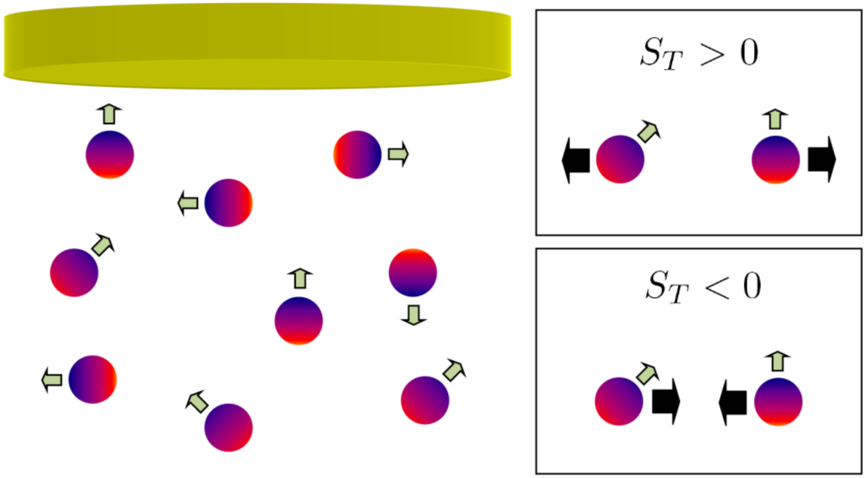
$$v_0 = \frac{\epsilon I D_T}{6\kappa}$$

- Inter-colloid Interaction

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

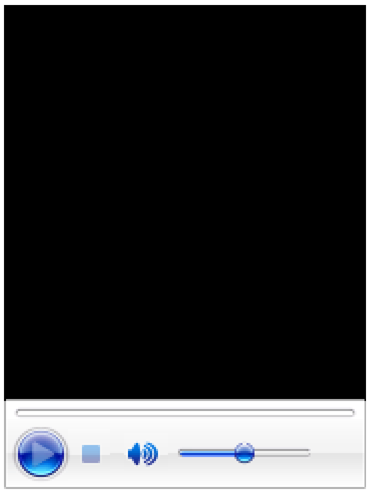
  - Thermo-repulsive
  - Thermo-attractive

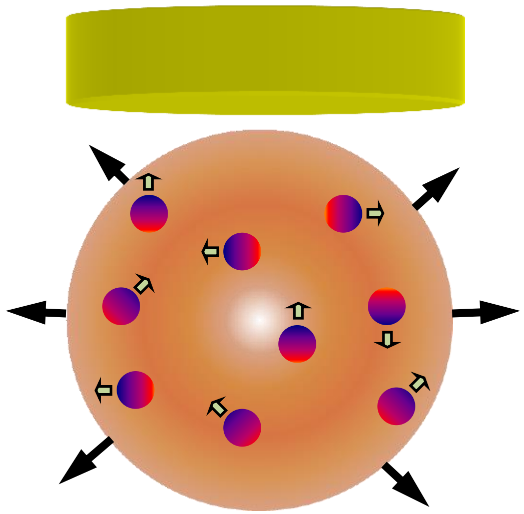
$$S_T = \frac{D_T}{D}$$

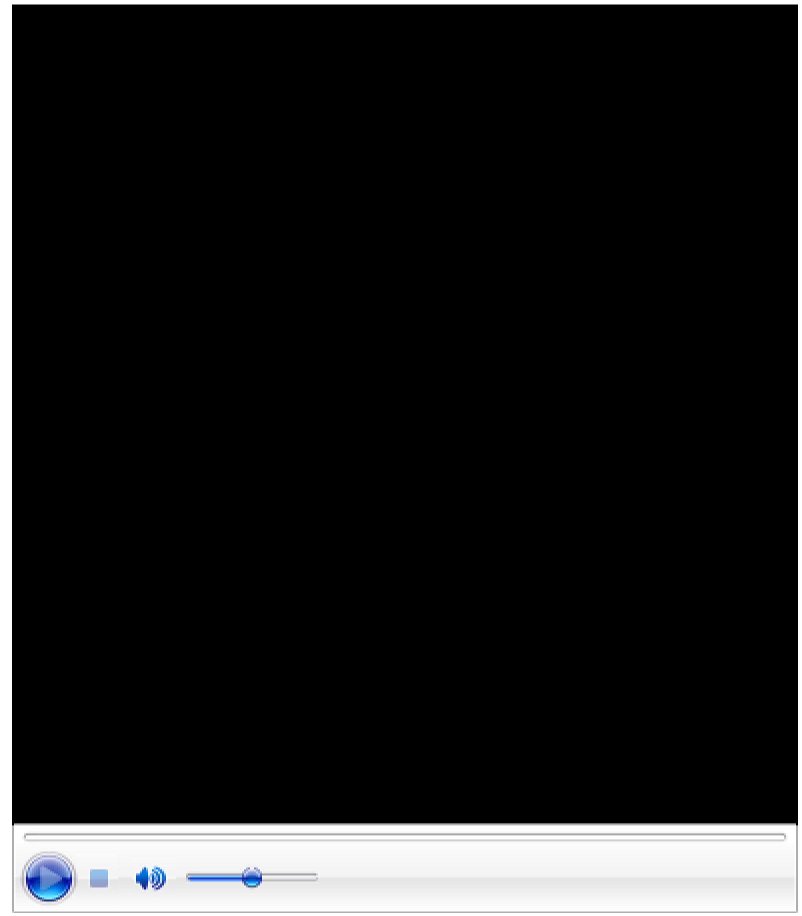


Golestanian (2012)

Thermo-Attractive (“Gravitational”) Case



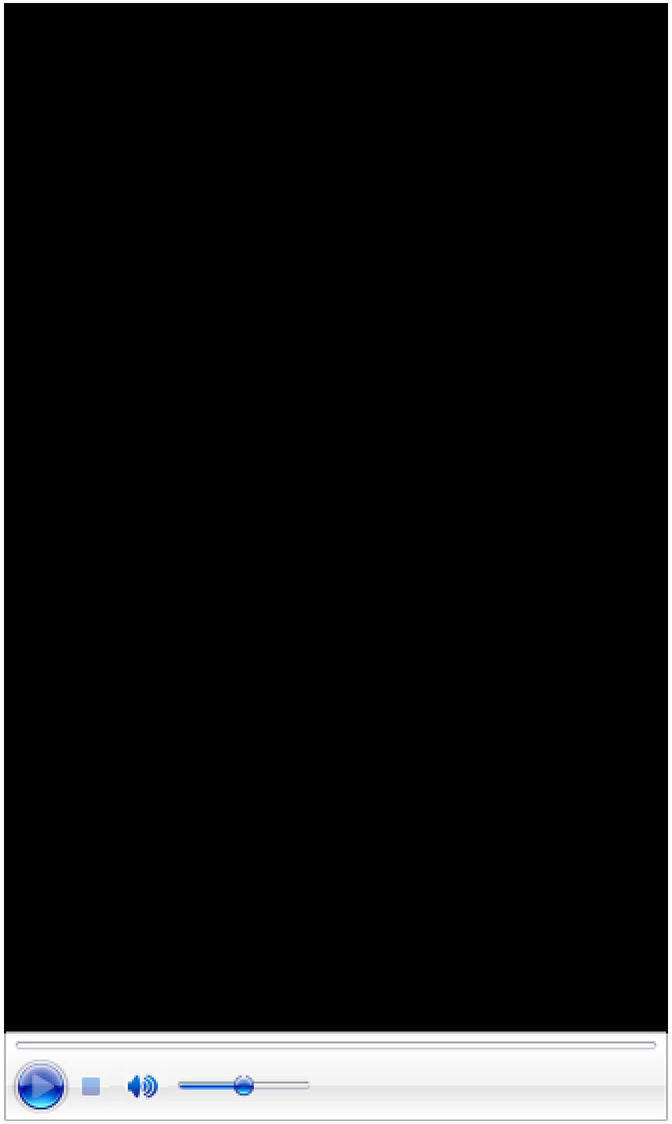




- Heat flux at the boundary cannot balance the heat generated inside -> uncontrolled build-up of heat
- In molecular systems: exothermic combustion reactions -> thermal explosion!

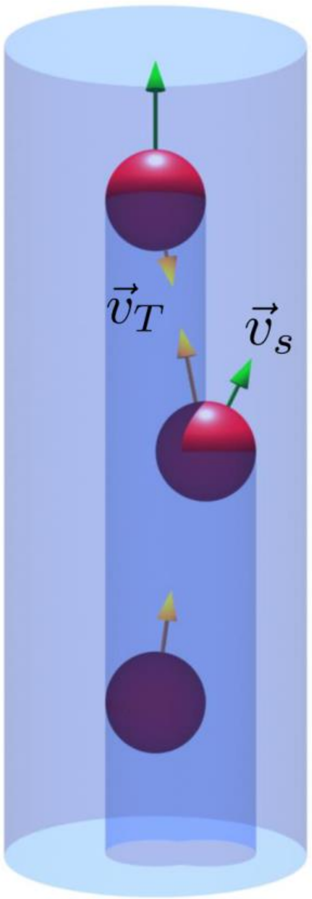
D.A. Frank-Kamenetskii, “Calculation of thermal explosion limits.” Acta. Phys. Chin., URSS **10**, 365-370 (1939)

A More Realistic Description



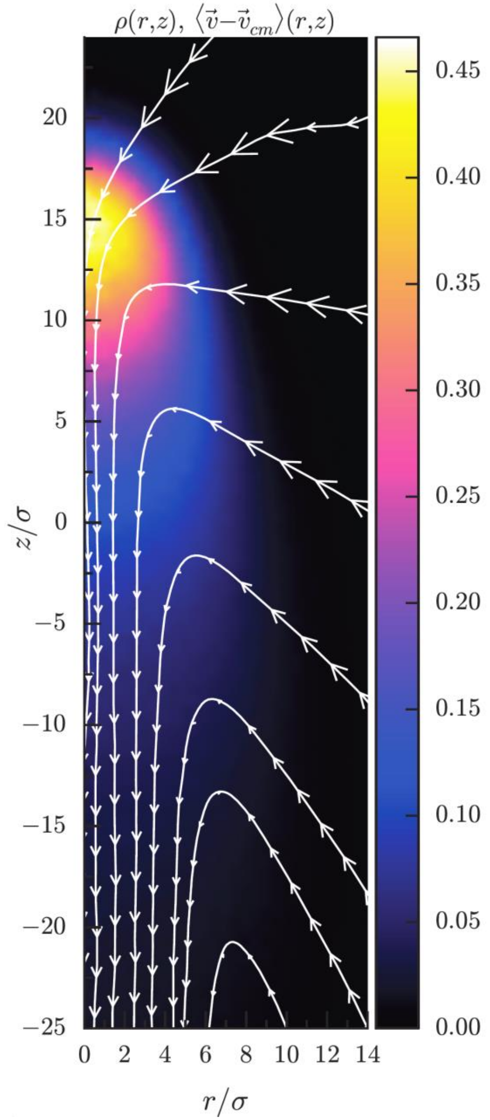
- Photo-taxis
- Attraction
- Excluded volume
- Shadowing

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

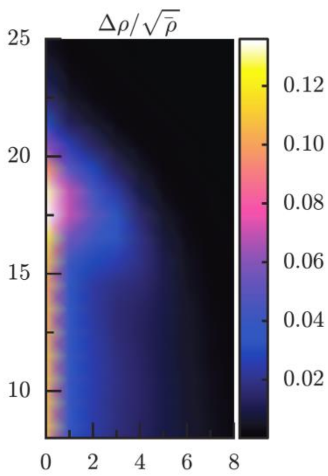


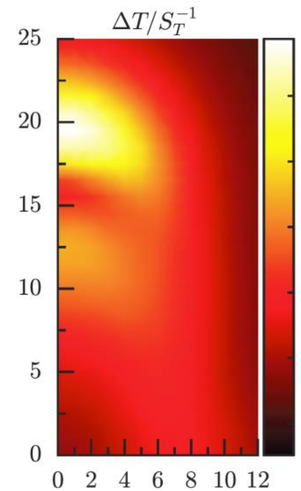
Cohen & Golestanian (2014)

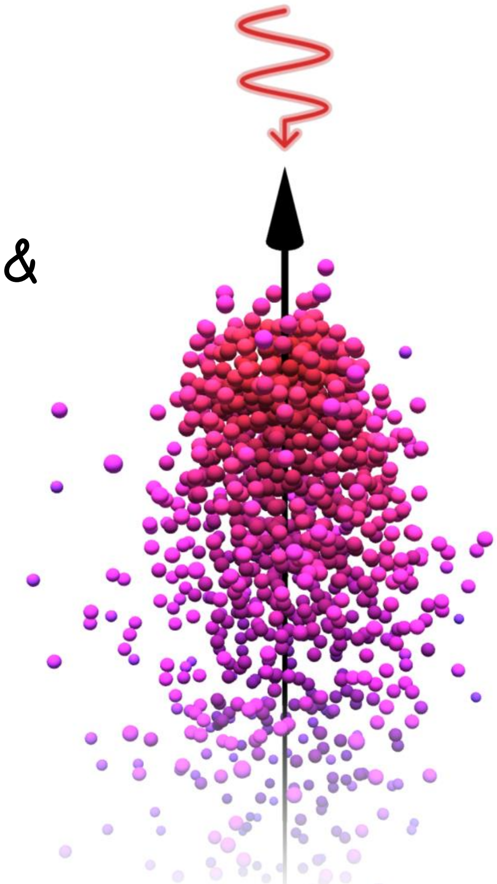
Comet-like Swarming



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





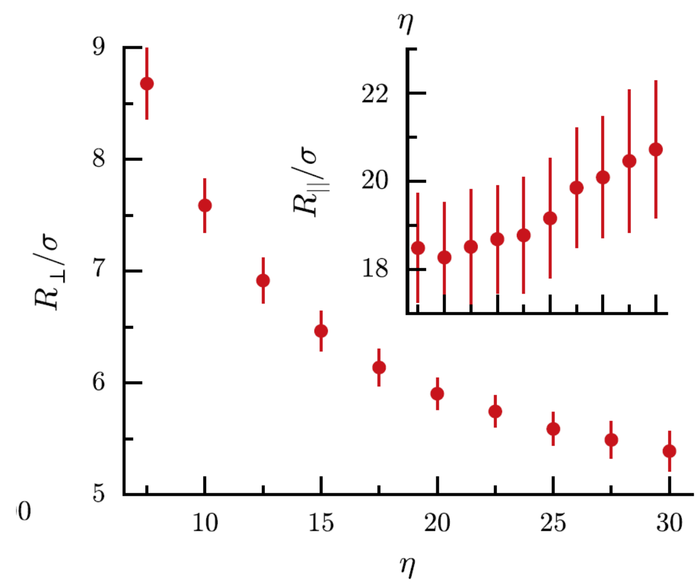


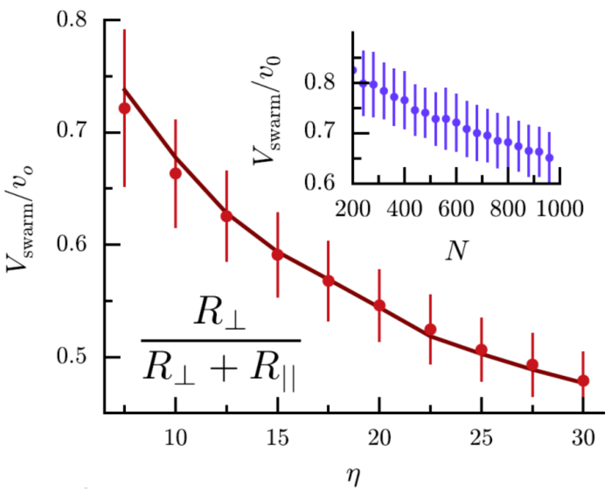
Changing the Coupling Strength

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

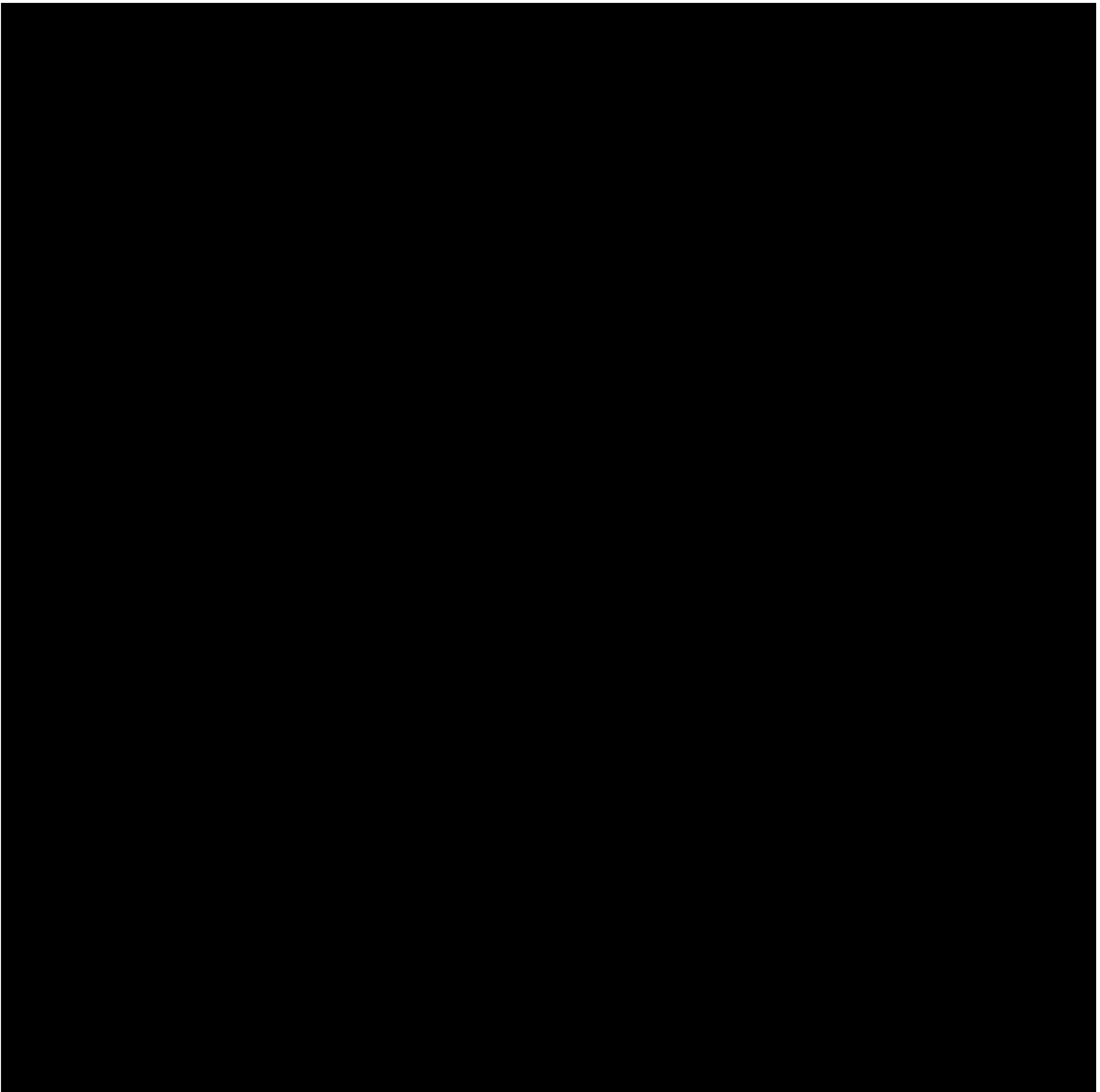
As the coupling strength increases, the Swarm:

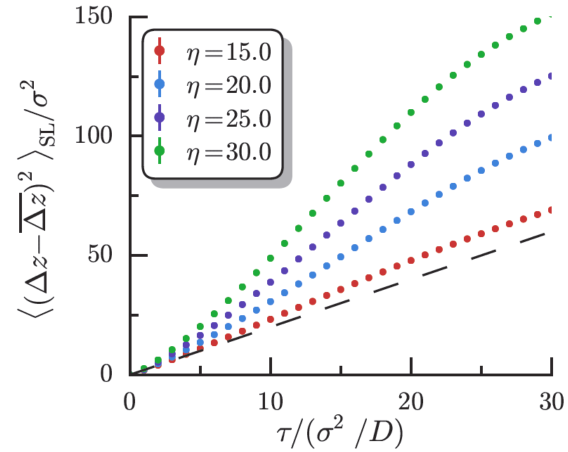
- elongates
- narrows down
- slows down
- becomes more dynamic

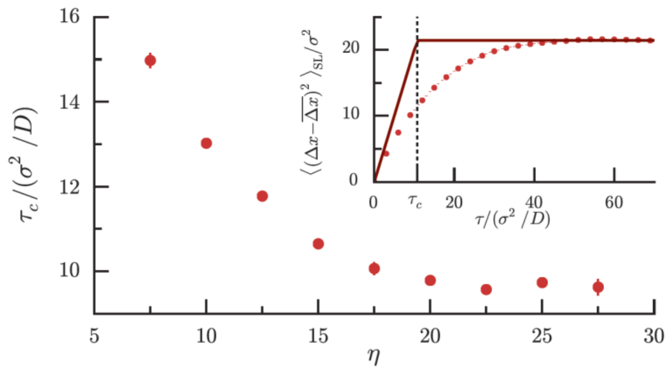




Particle Tracking: Confinement

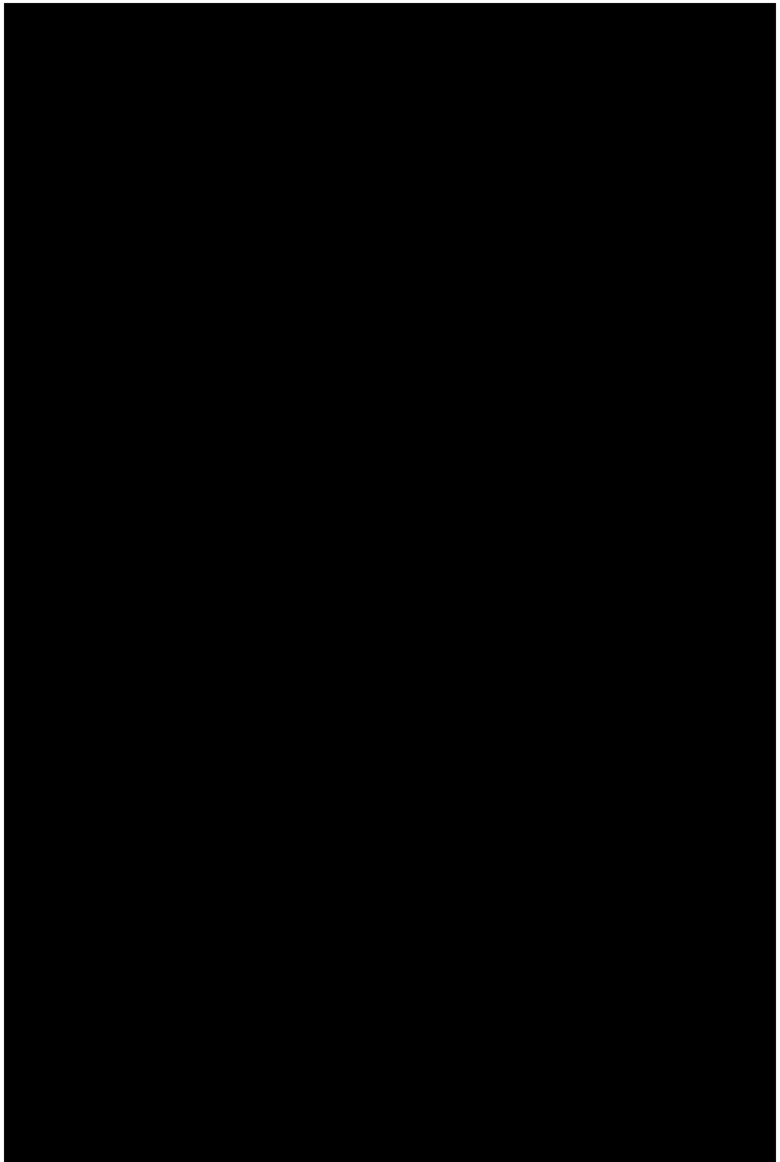


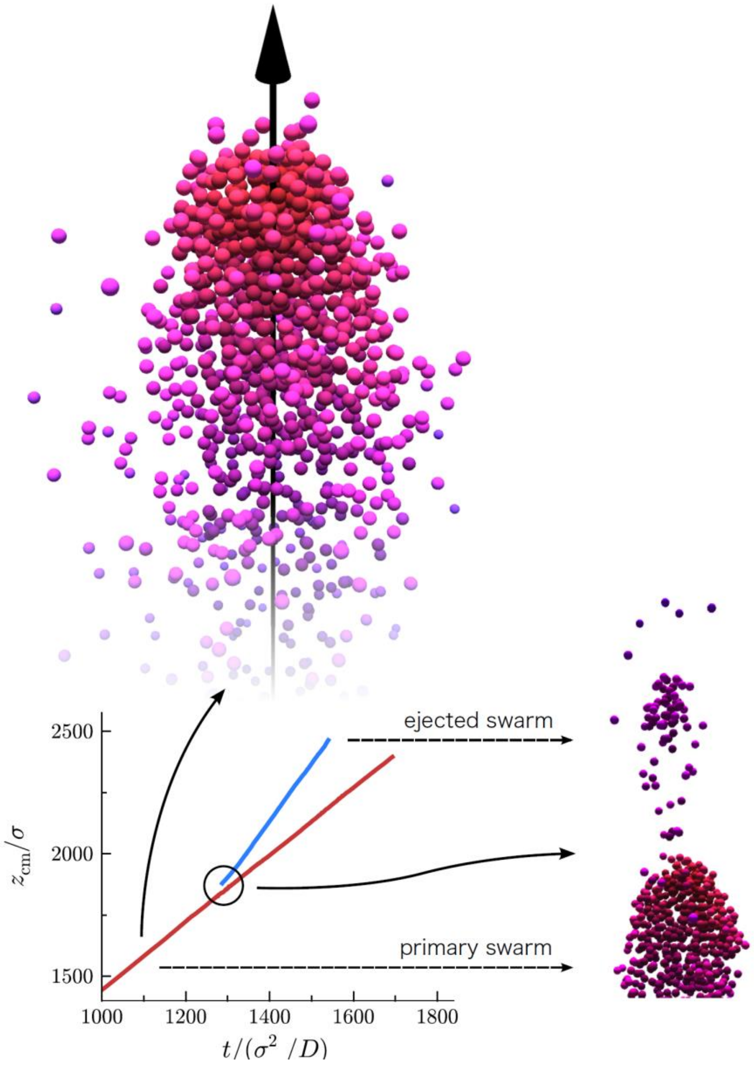




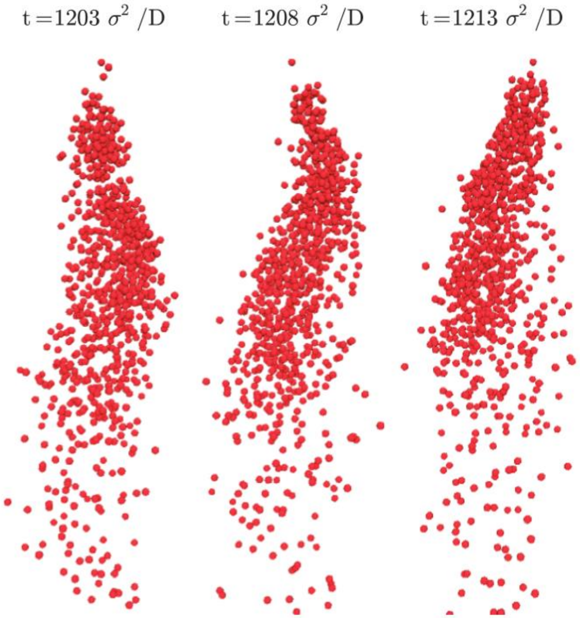
Jack Cohen

Increased Coupling Behaviour: Fission

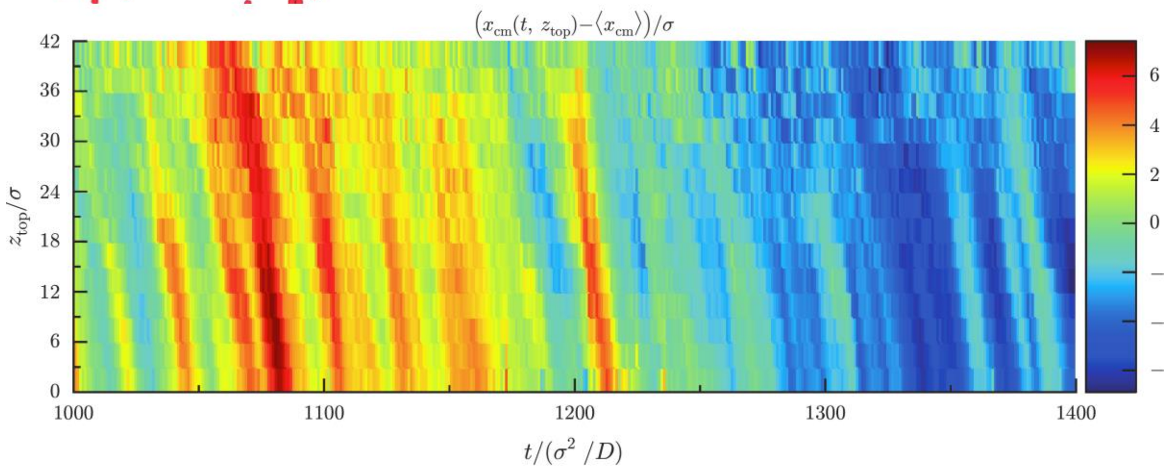




Increased Coupling Behaviour: Waves



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



Conclusion

- Colloids can be made **active**, i.e. driven out of equilibrium, in a variety of ways…
- Active colloids will have self-propulsion, if they are "sufficiently asymmetric"
- Both self-propelled and symmetric active colloids perform anomalous stochastic motion depending on the time scale
- Collective behaviour of active colloids could be very rich due to the long-range nature of the their interactions