Collective behavior and pattern formation
in
actuated magnetic
and
Janus colloidal suspensions

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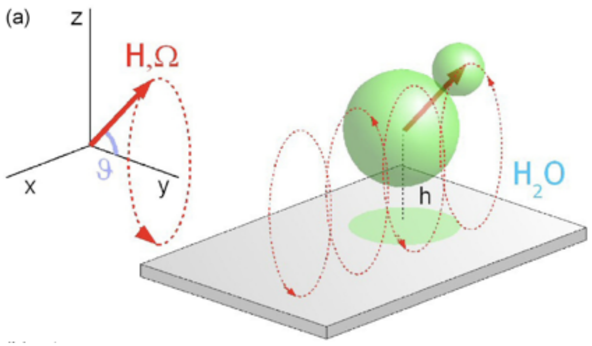
1. Introduction

2. Actuated paramagnetic colloids

3. Autocatalytic colloidal suspensions

4. Conclusions

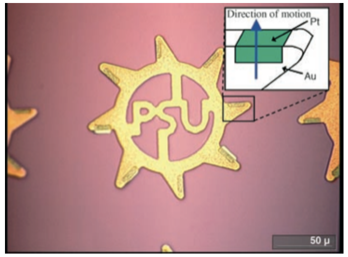
Actuated colloids

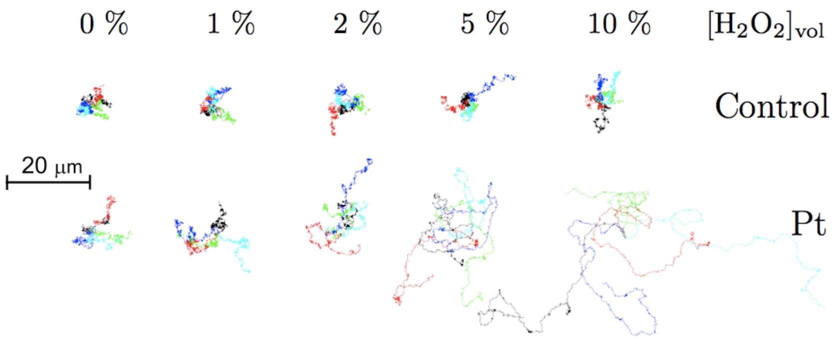


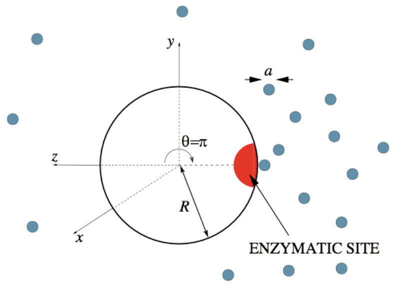
Self-propelled colloids

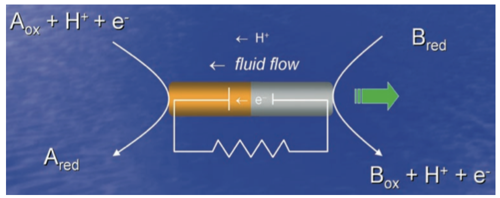
Adding reactivity:
new propelling mechanisms
Different sets of micro/nano robots

Heterogeneous particles
Confinement + asymmetric mobility
no deformation





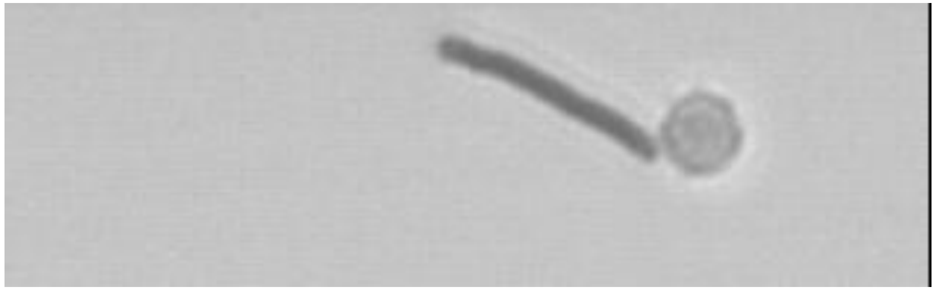




Magnetic field: Local acceleration

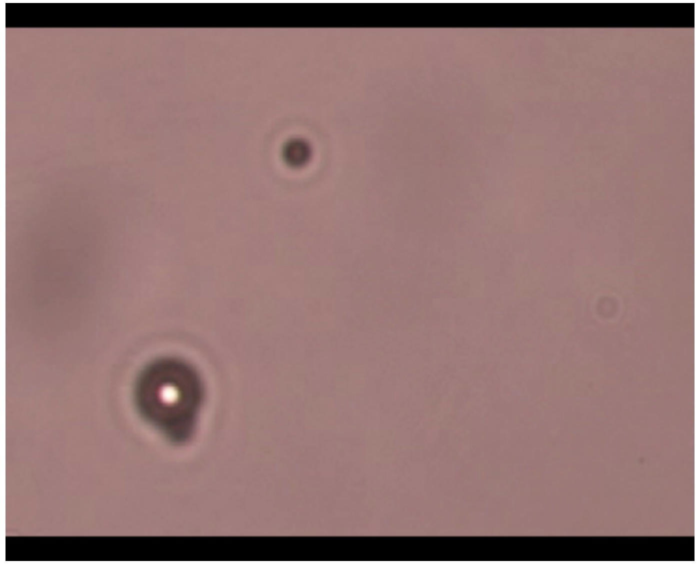
Top view

Asymmetry + local bending: wave

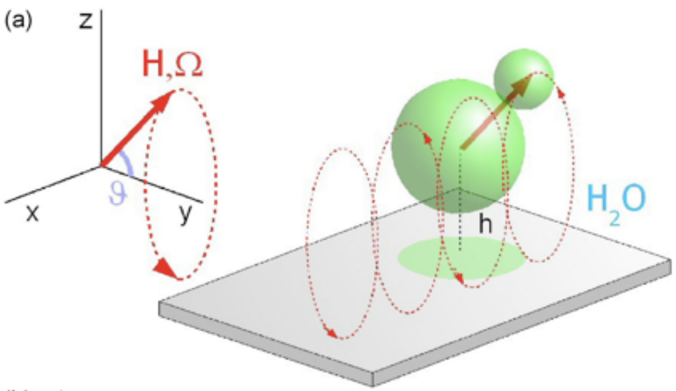


Bibette et al

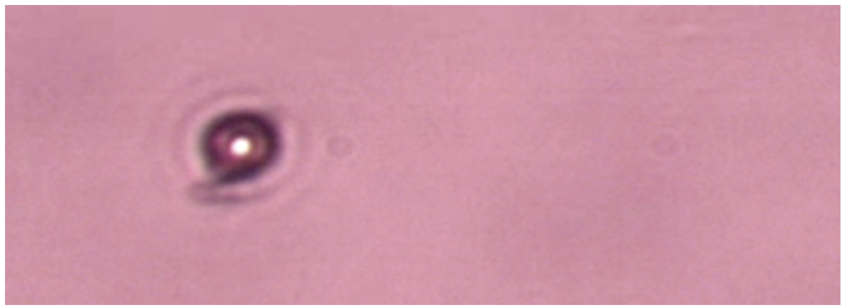
Doublet vs isolated



Confinement + asymmetric mobility
no deformation

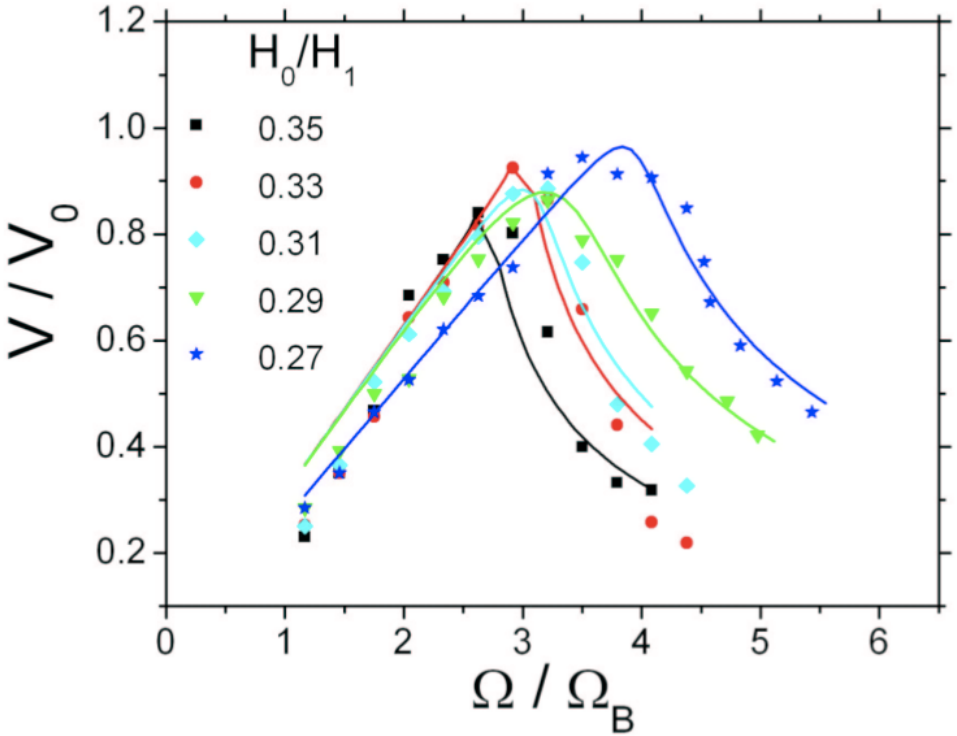


Larger aggregate

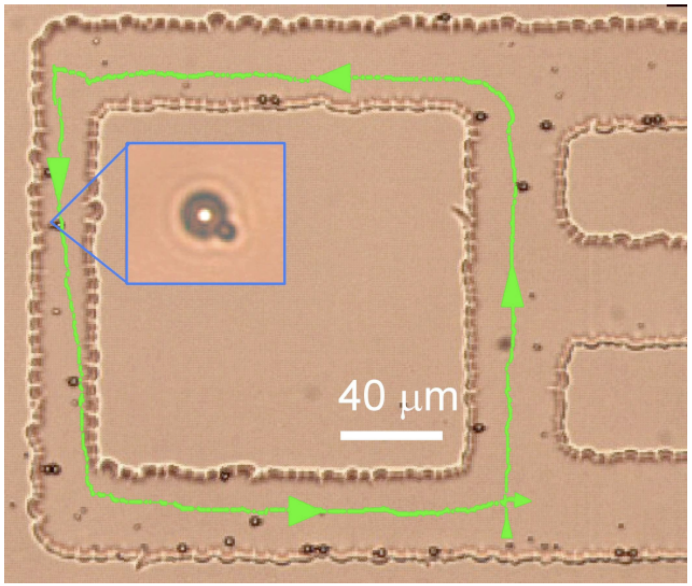


Tierno et al

Good agreement



Fitting: height
rotational friction



Low Ω: increase rectification rate
change in orientation negligible

High Ω: doublet aligns parallel to wall
decrease in asymmetry

Controlled motion in microfluidic devices

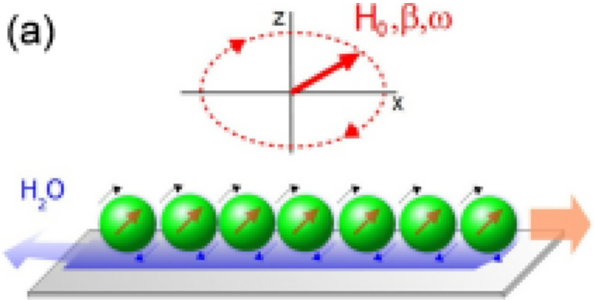
Free colloids

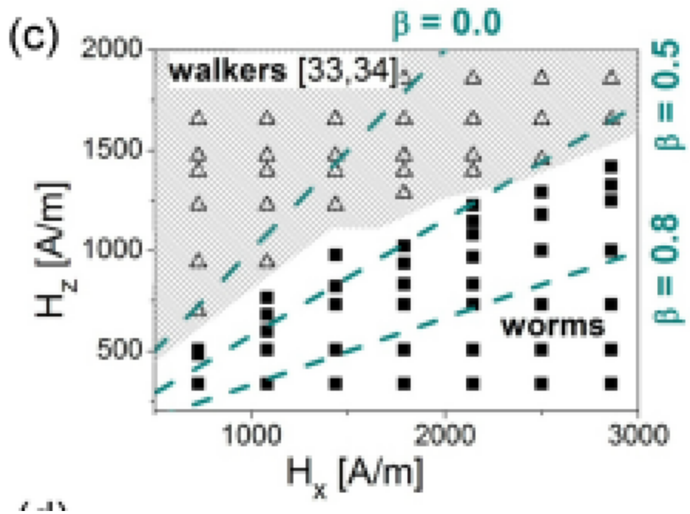
Self-assemble

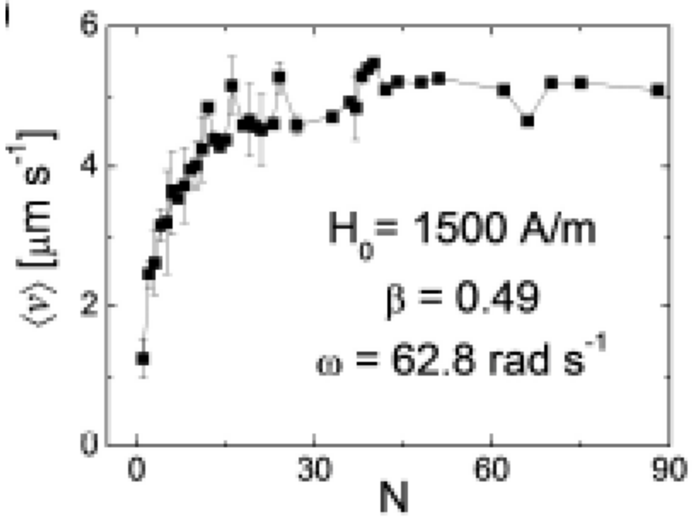
Dipolar interactions

Modes of motion

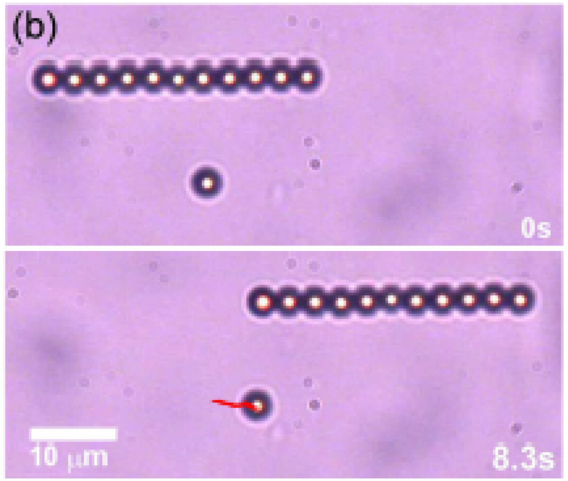
Sensitive to geometry







Enhanced velocity with worm size



Free colloids

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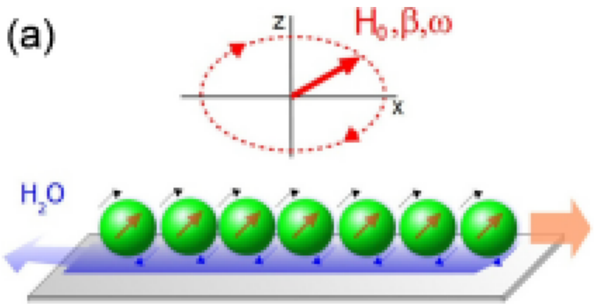

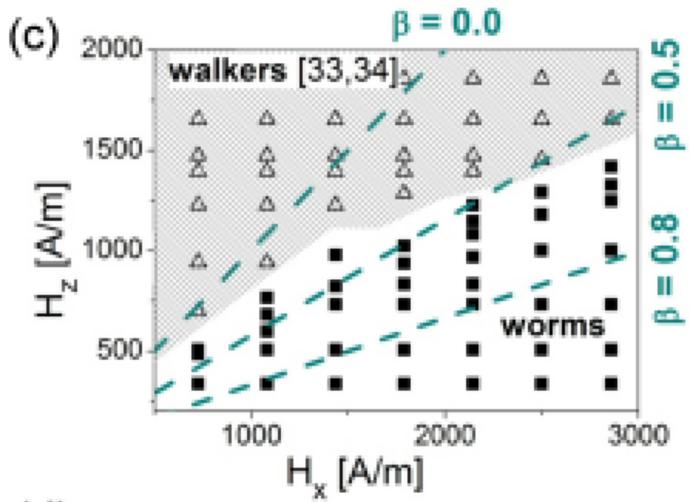

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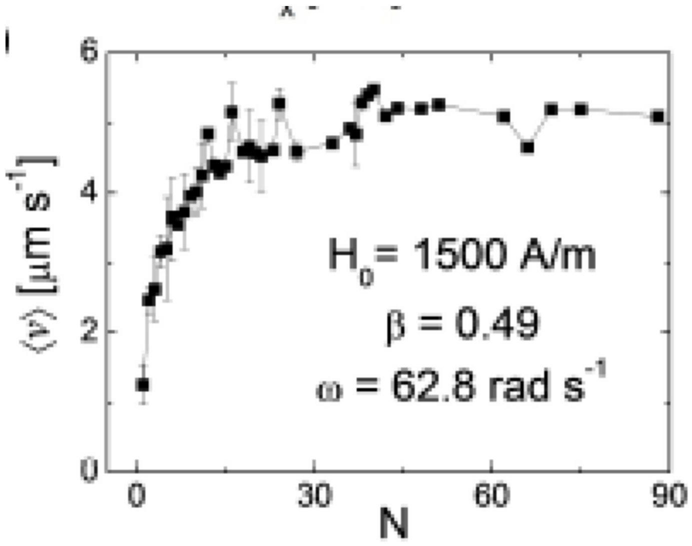
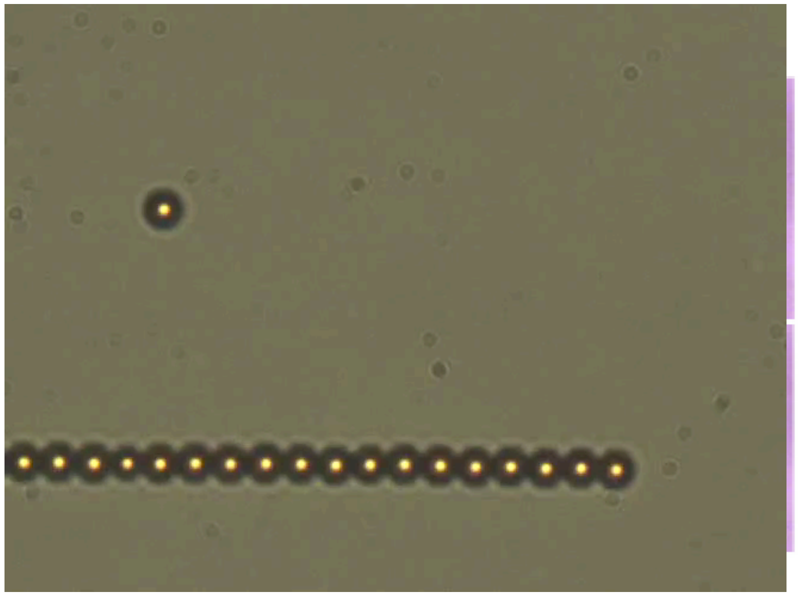




Hydrodynamic theory

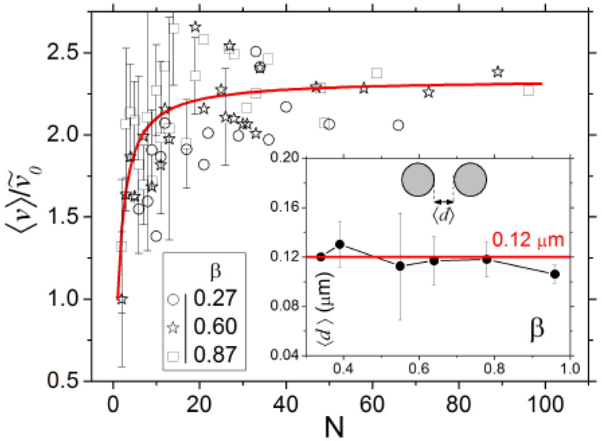
Stresses induced by images

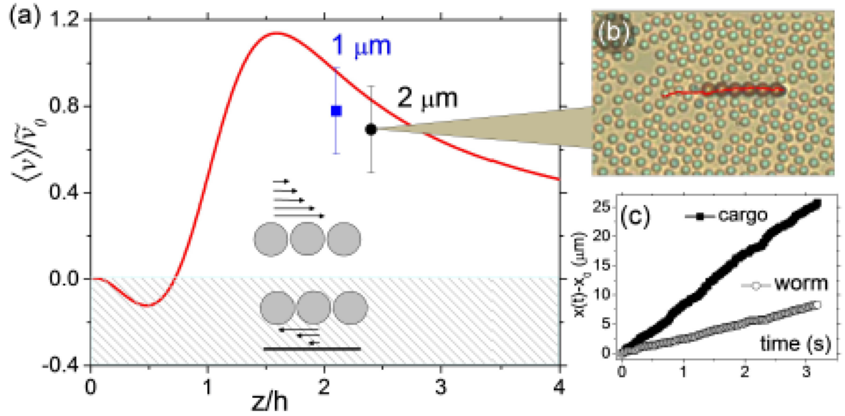
$$\mathbf{v}_{CM} = v_0\mathbf{e}_x + \frac{|v_0|}{N}\sum_{j=0}^{N}\sum_{i\neq j}\left\{-\frac{1-\chi}{[1+\epsilon^2(i-j)^2]^{3/2}} + \chi\frac{6\epsilon^2(i-j)^2}{[1+\epsilon^2(i-j)^2]^{5/2}}\right\}\mathbf{e}_x$$

Predicts

Enhancement

Saturation



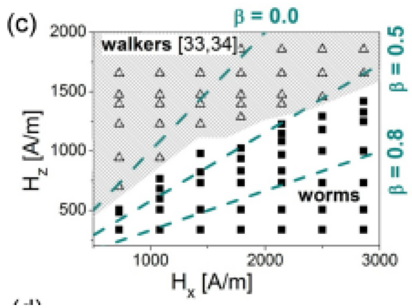


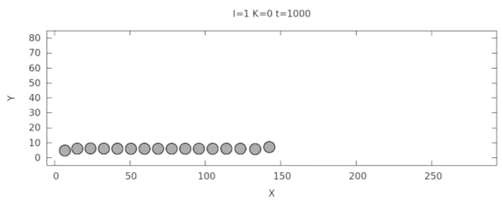
Colloidal conveyor belt

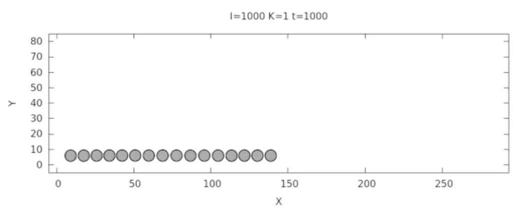
Higher speed above the aggregate

Generalized phase diagram

relevant dimensionless parameters

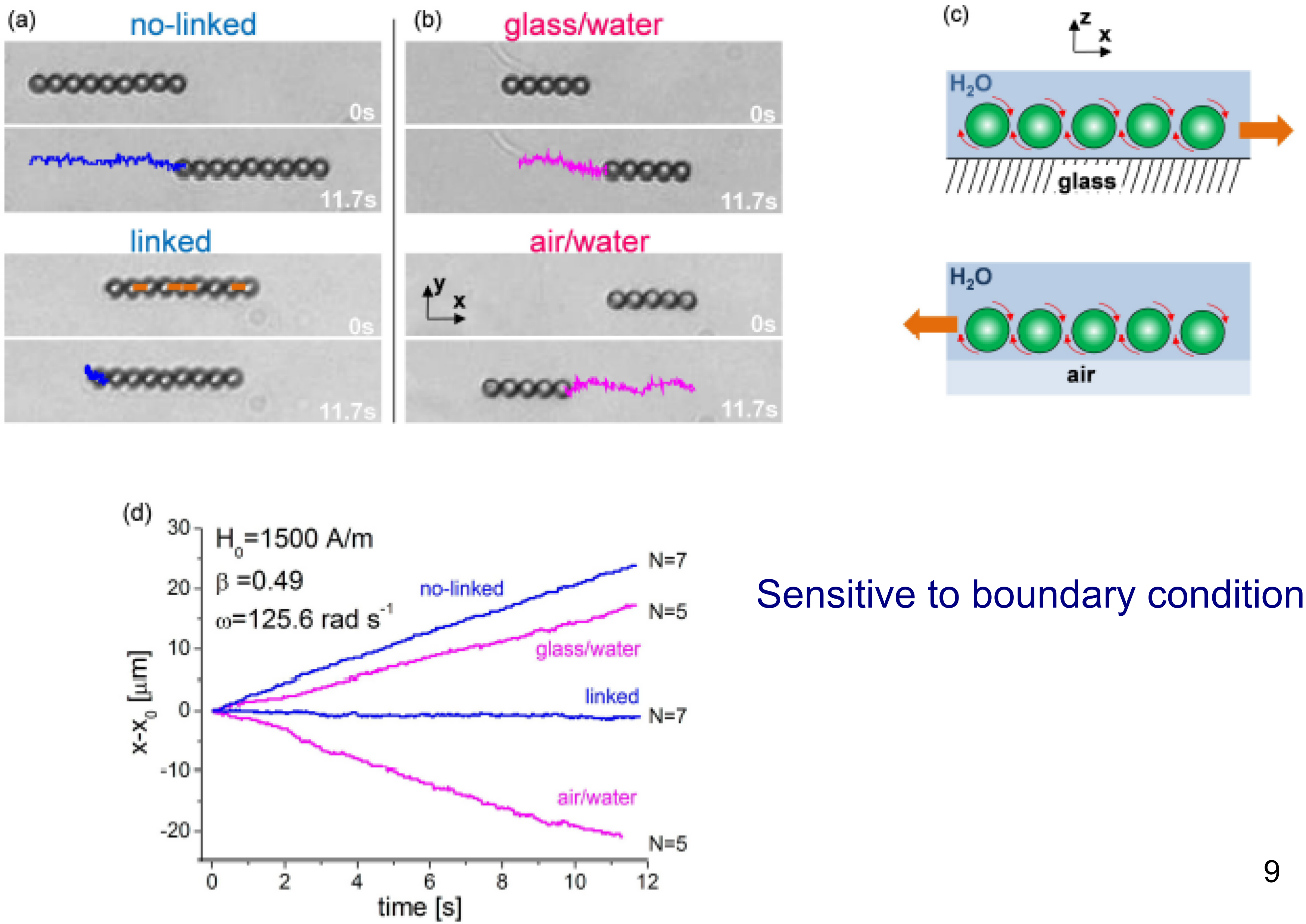






Morphological transitions

Hydrodynamic coupling

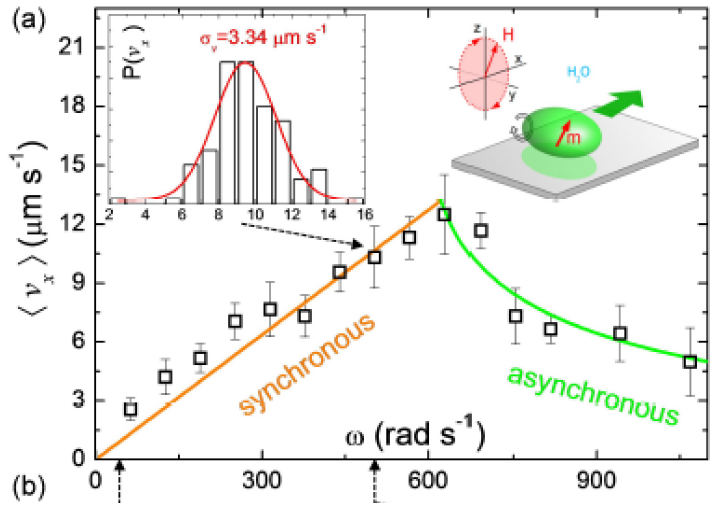


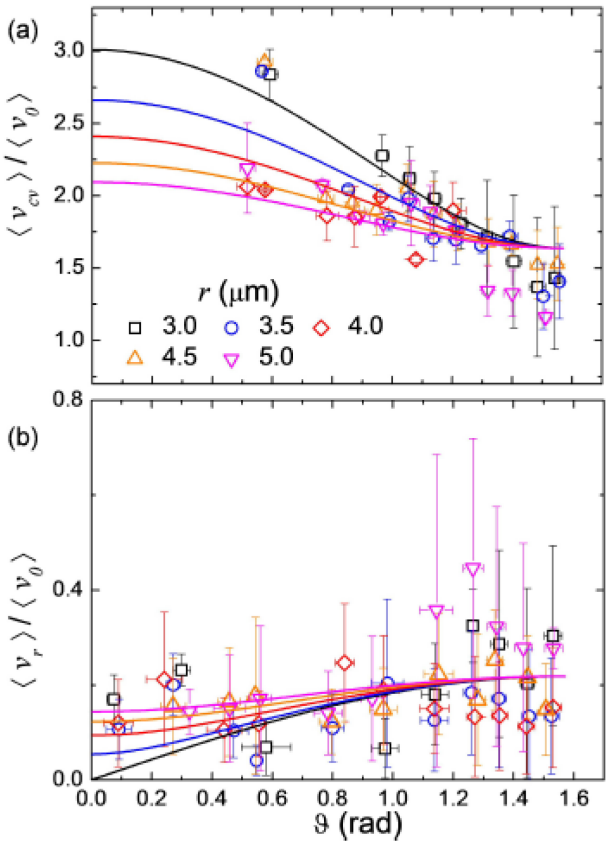
Sensitive to boundary conditions

Pairs of rotating paramagnetic colloids

Negligible dipolar interaction

Hydrodynamic rotors





Supporting video 1

Magnetic field parameters:

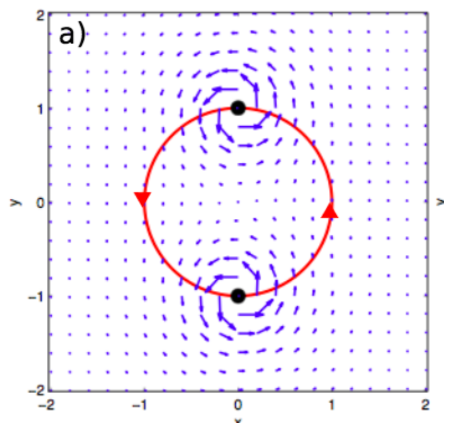
H_0 = 4400 A/m

Top: ω =31.4 rad/s

Bottom: ω =502.6 rad/s

Far field assumption

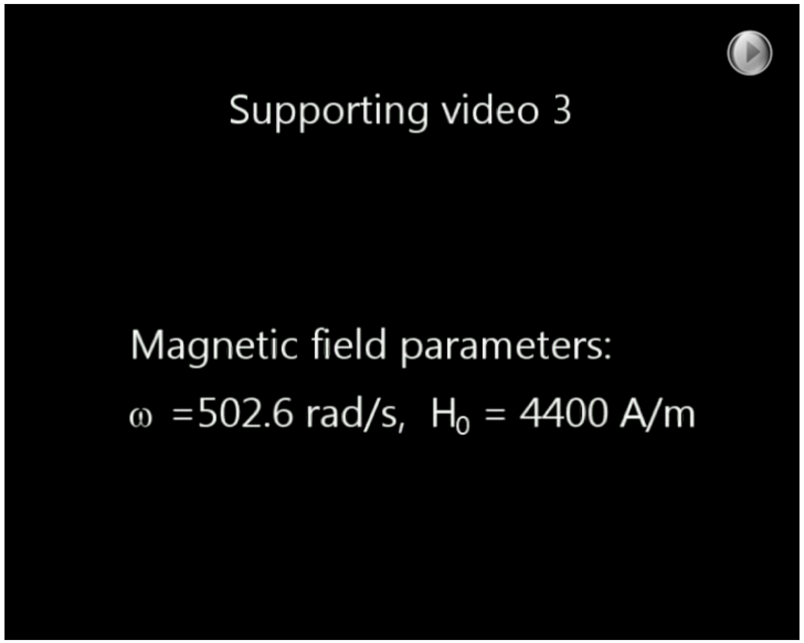
Fixed points unstable

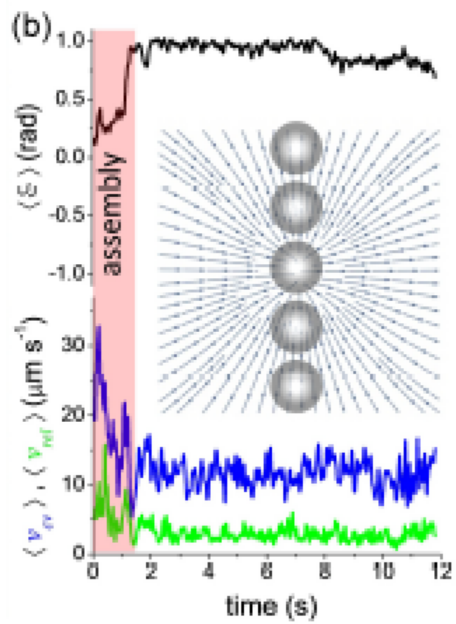


Bound trajectories

net displacement

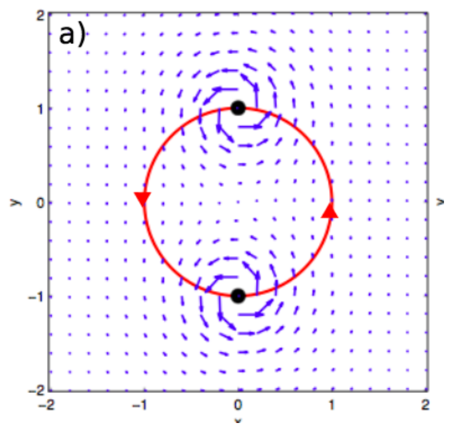
wall-distorted?





Larger self-assemblies

periodic trajectories



Far field assumption

Fixed points unstable

Bound trajectories

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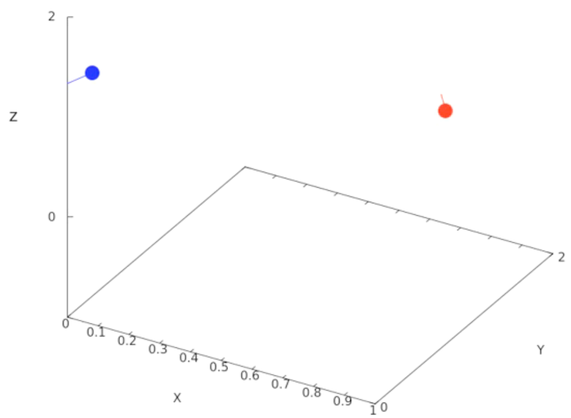
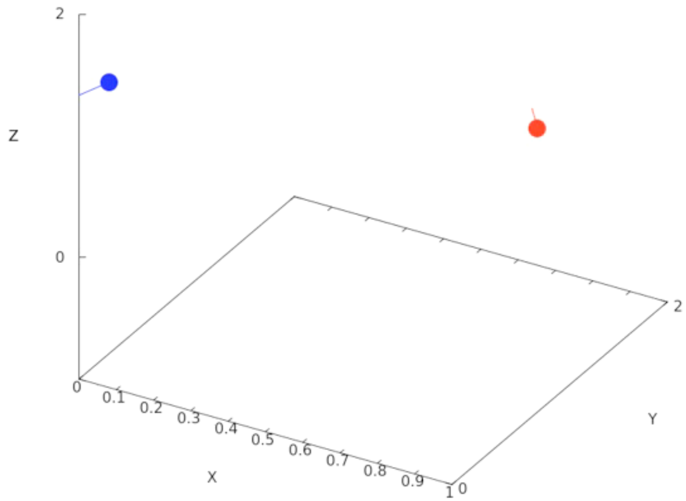
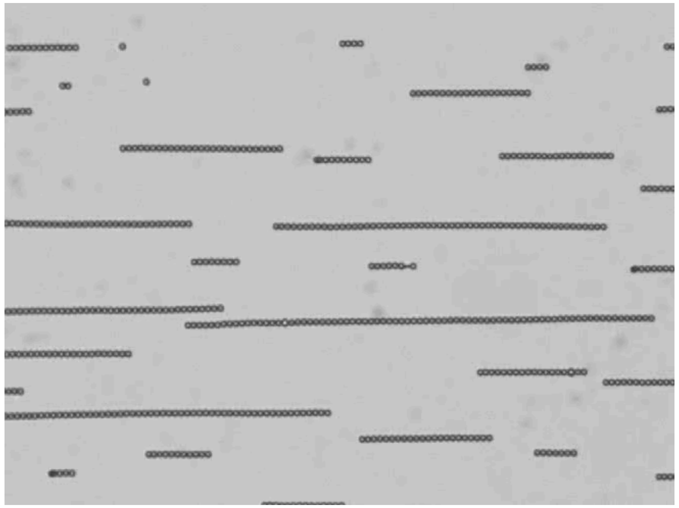
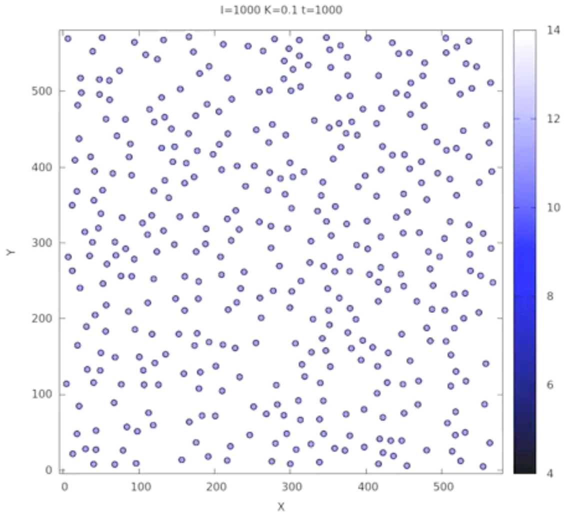


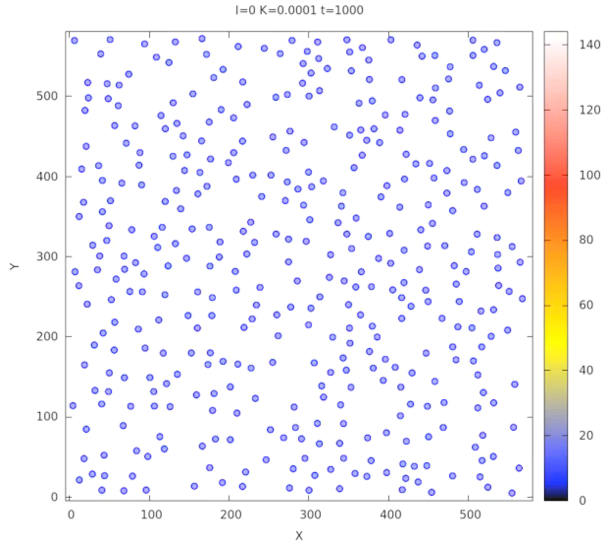


Generalized phase diagram

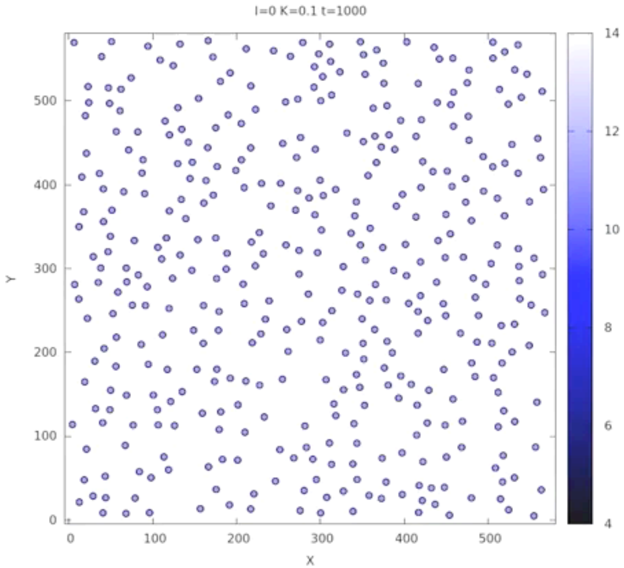
Identified relevant dimensionless parameters

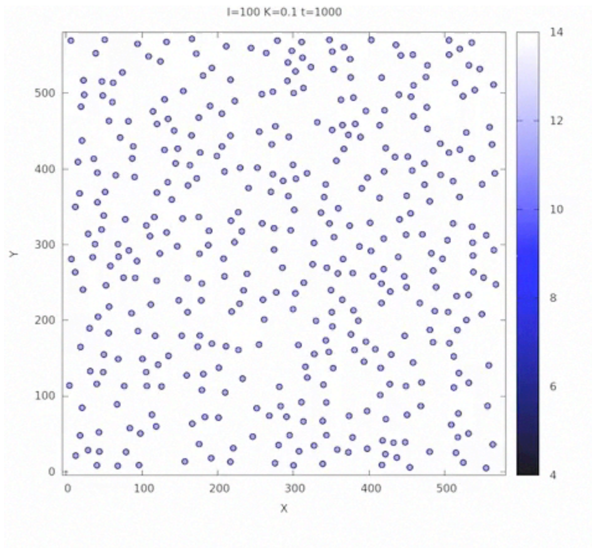






Morphological transitions

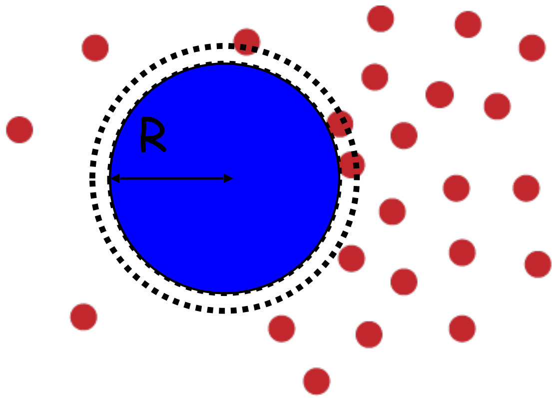




Colloidal phoresis

multiscale "transport phenomenon"

$$\mathbf{v}(\mathbf{r}_S) = \mu(\mathbf{r}_S)(\mathbf{I} - \hat{\mathbf{n}} \otimes \hat{\mathbf{n}})\nabla\phi(\mathbf{r}_S)$$



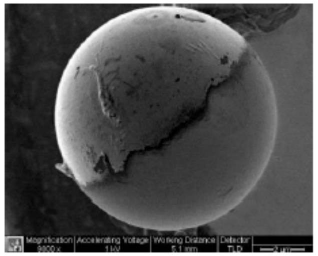
surface phoretic mobility

$$\mu(\mathbf{r}_S) = \frac{k_B T}{\eta} \int_0^\infty r \left[1 - \exp(-\Psi(\mathbf{r})/k_B T)\right] dr$$

colloid/solute interaction potential (short-ranged)

velocity of a (spherical) particle of radius R

$$\mathbf{V} = -\frac{1}{4\pi R^2} \int\int_\Sigma \mu(\mathbf{r}_S)(\mathbf{I} - \hat{n} \otimes \hat{n})\nabla\phi(\mathbf{r}_S) d\mathbf{r}_S$$



http://www.mems.duke.edu/fds/pratt/MEMS/faculty/benjamin.yellen

$$\alpha(\mathbf{r}) = \alpha_0 H\left(\theta - \frac{\pi}{2}\right)$$

$$\phi(\mathbf{r}, t) \rightarrow \phi(\mathbf{r}, t) - \alpha(\mathbf{r})\phi(\mathbf{r}, t)$$

→ self-propulsion

Colloidal phoresis

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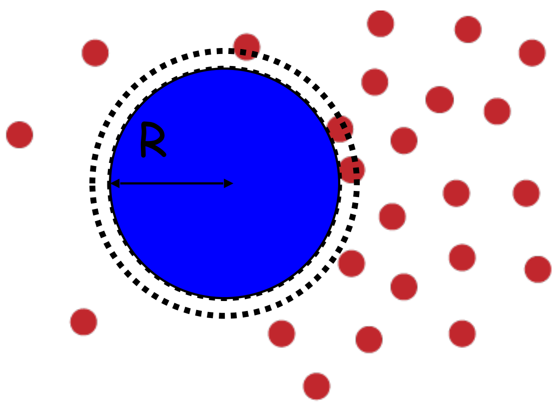

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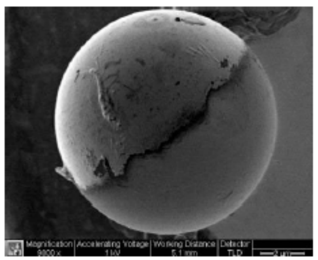

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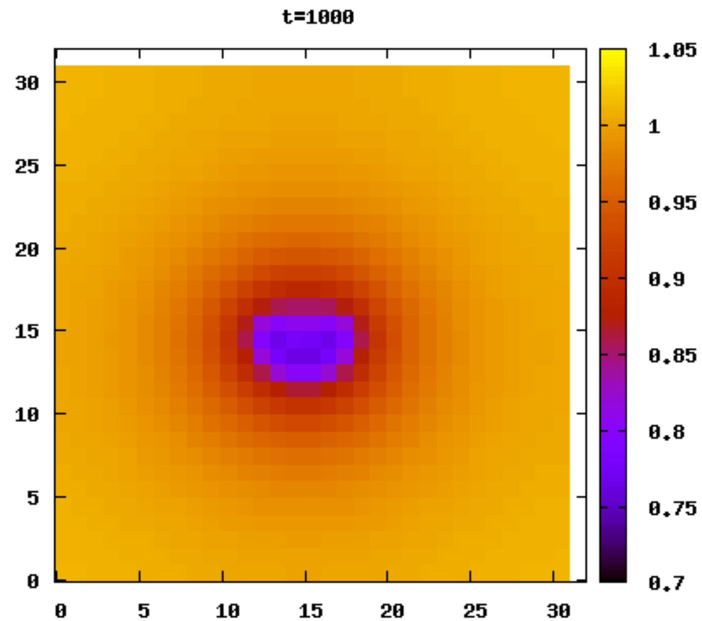

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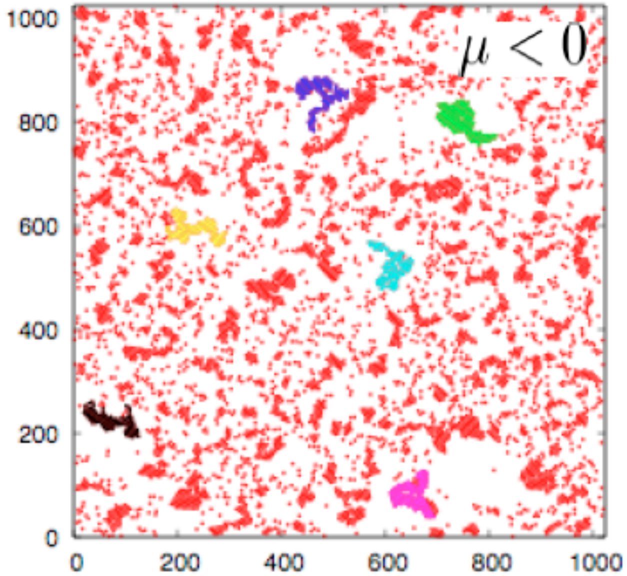
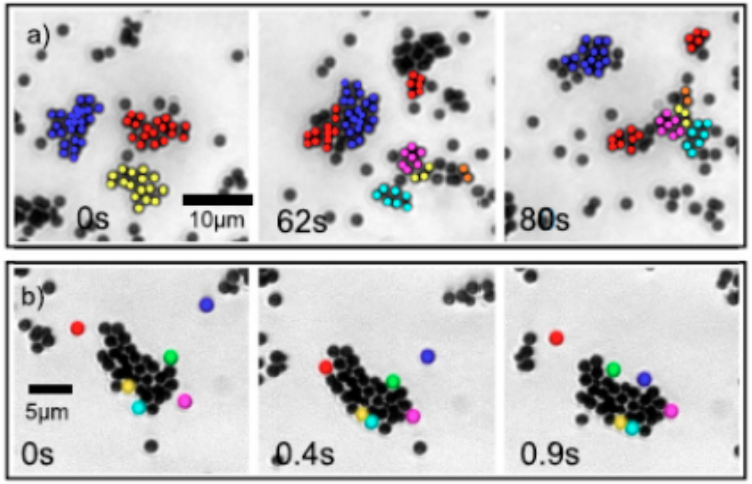
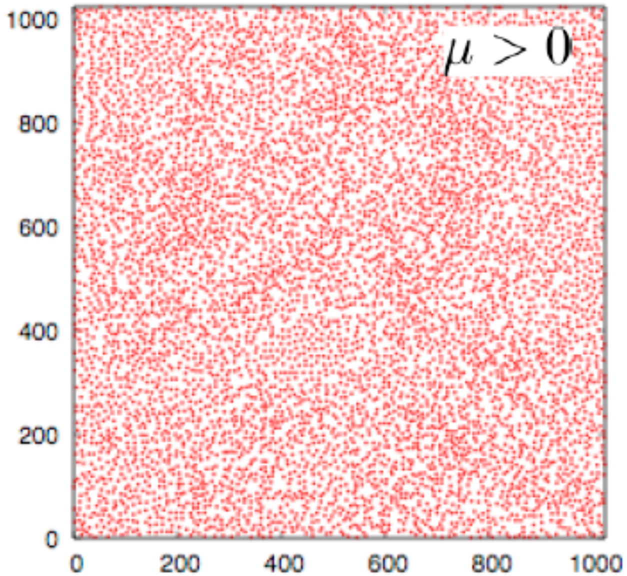
self-propulsion

Collective dynamics in “2D”: phoretic mobility?

Teurkhauff et al. PRL (2012)



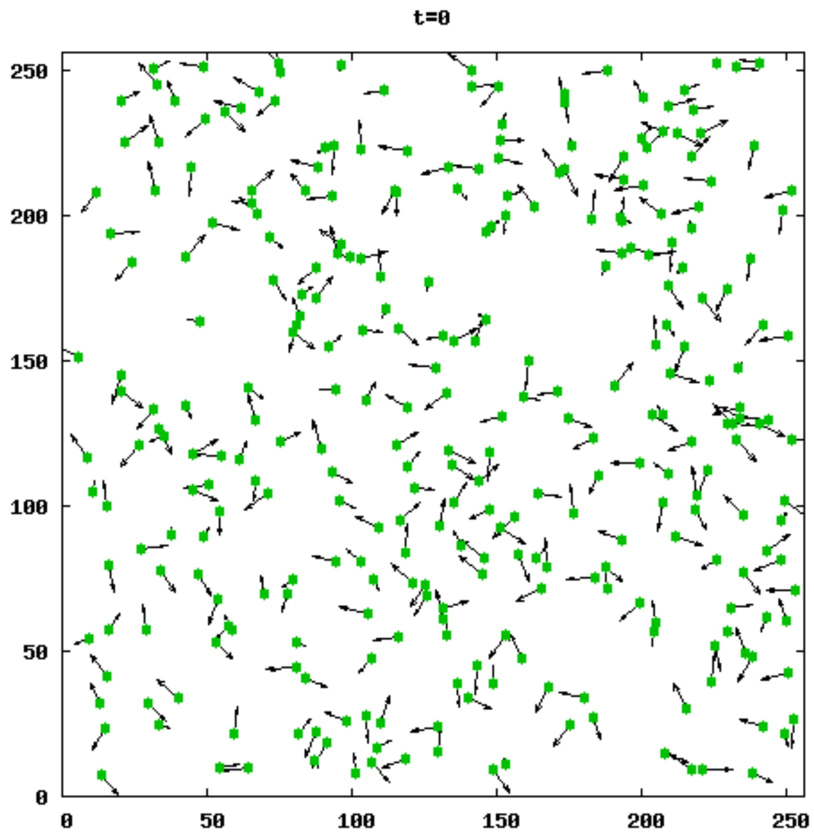


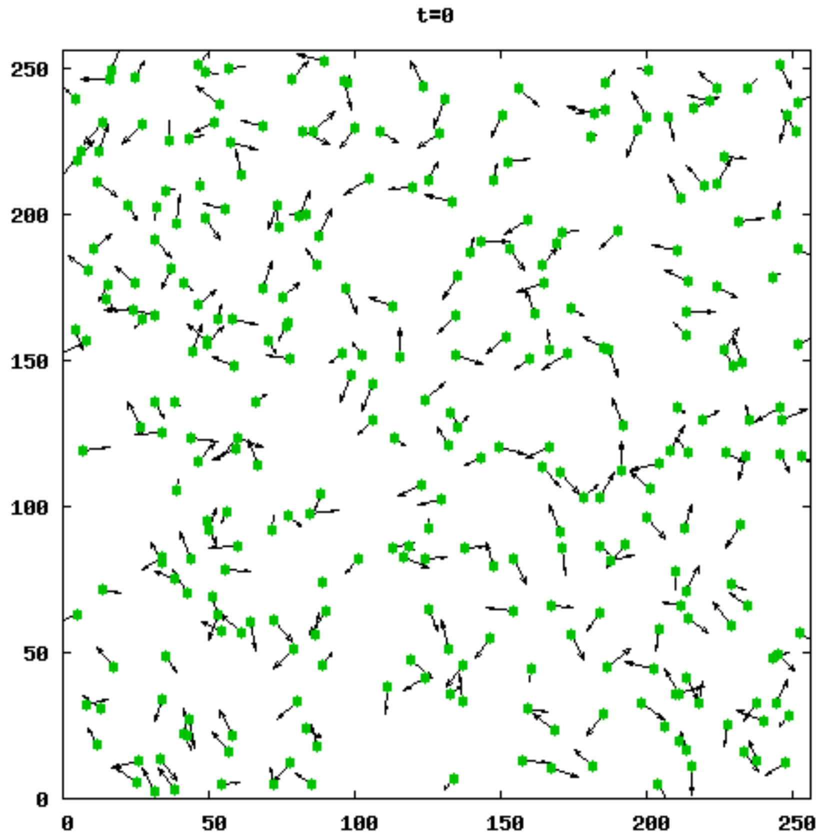


Palacci et al. Science (2013)

Attractive chemical swimmers

No hydrodynamics



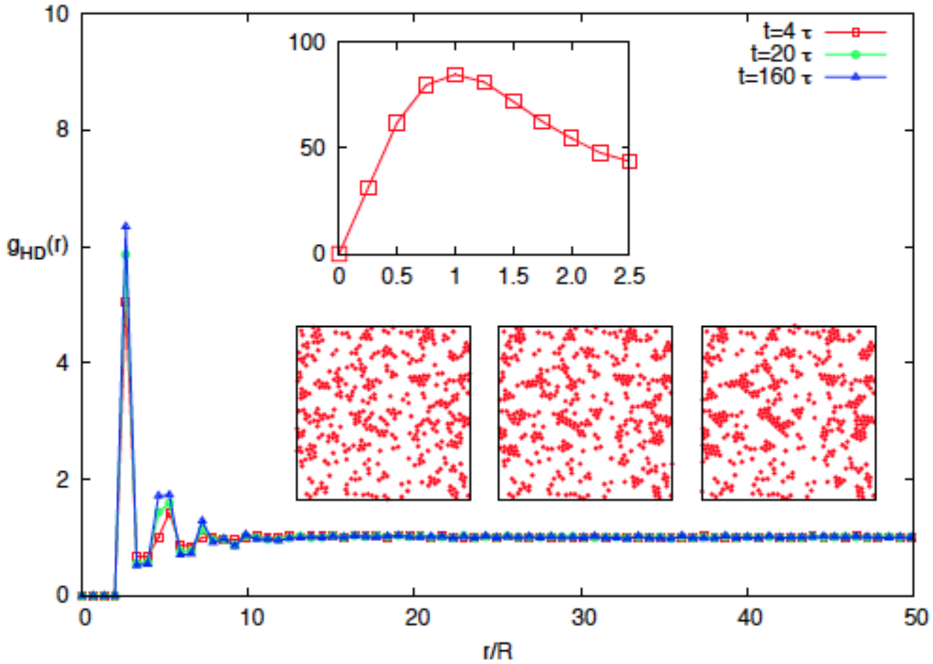


Cluster formation

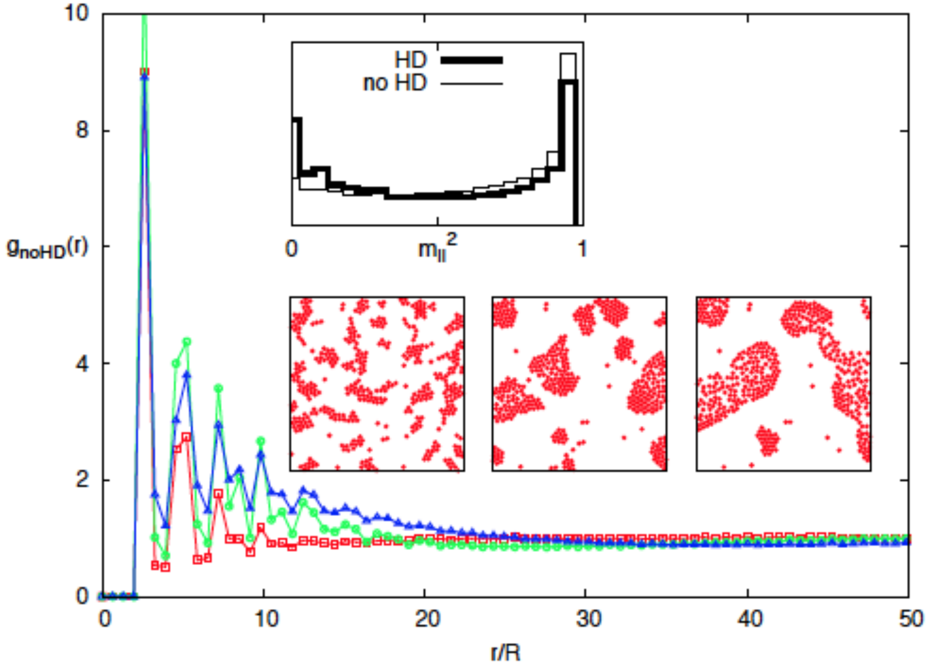
Self assembled structured
Radial distribution functions

Clustering regime $\mu = -0.5$

With hydrodynamics



Without hydrodynamics



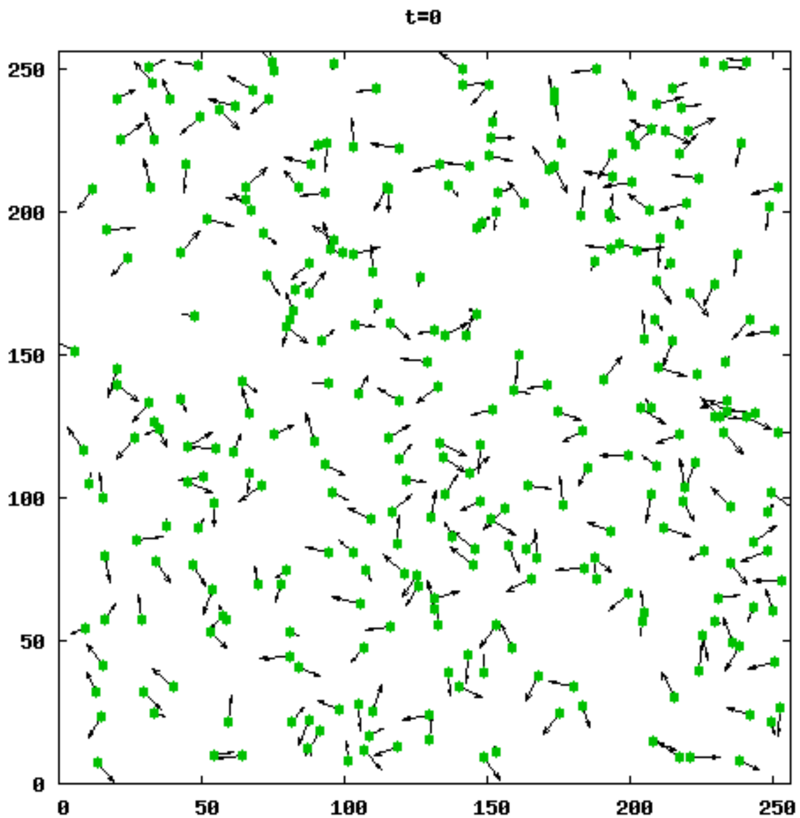
$$\mathcal{D}(\tilde{t}) = \int_0^\infty \left(g_{HD}(r,\tilde{t}) - g_{noHD}(r,\tilde{t})\right)^2 dr$$

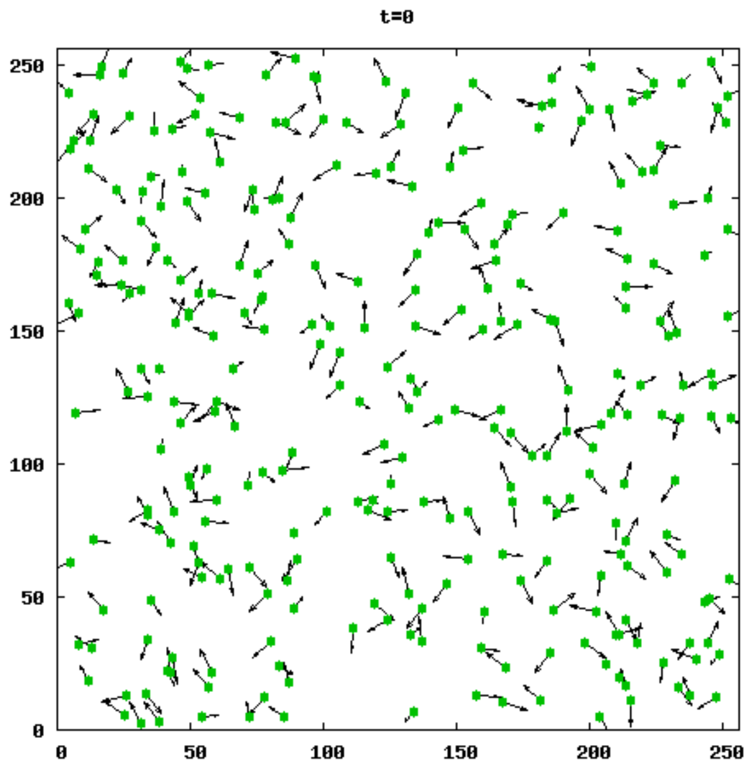
No Hydro: larger friction

$$\tau_f^{(HD)} \approx 5\tau_f^{(noHD)}$$

Repulsive chemical swimmers

No hydrodynamics





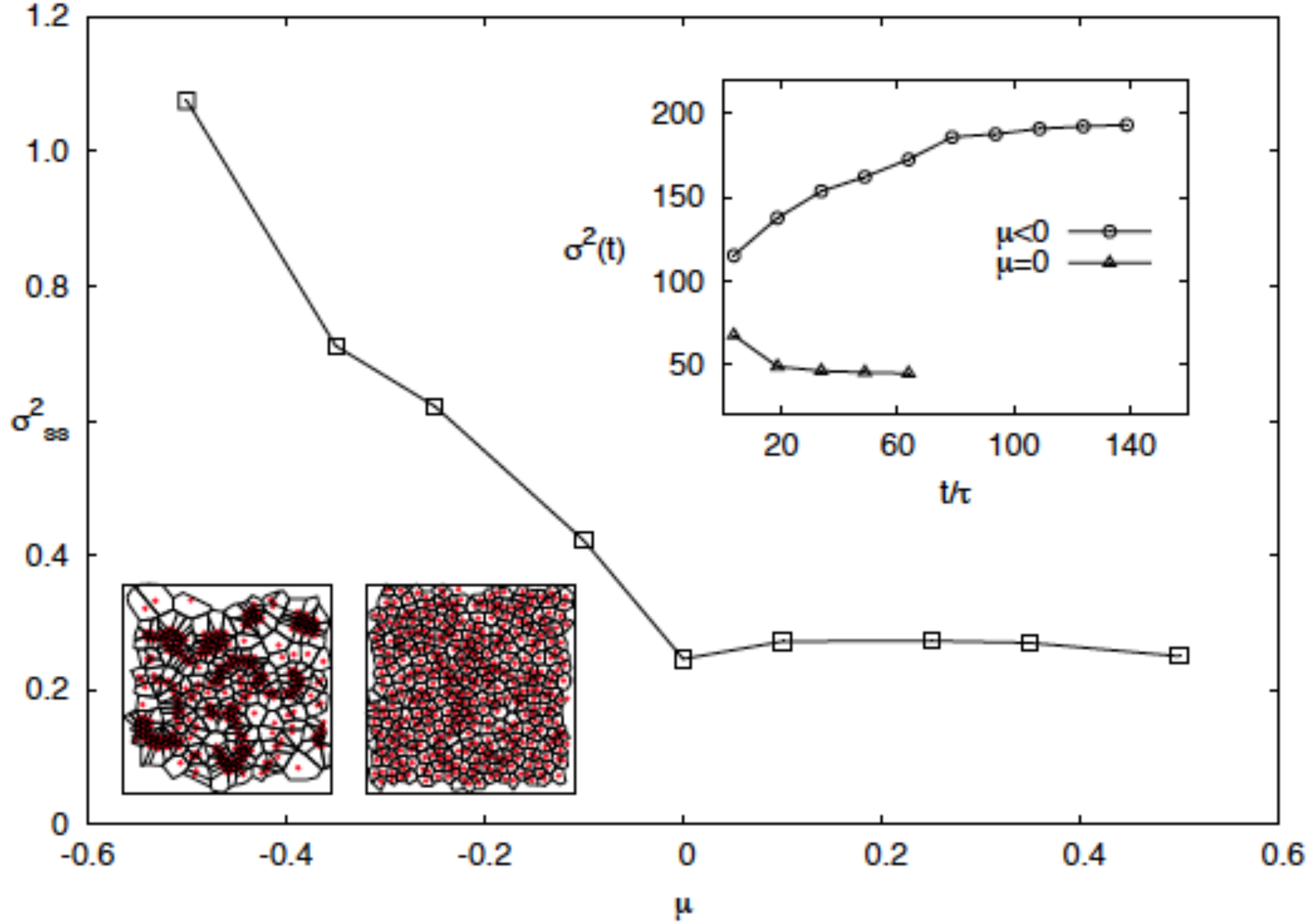
Towards a crystal structure

Faster dynamics
larger number of “defects”

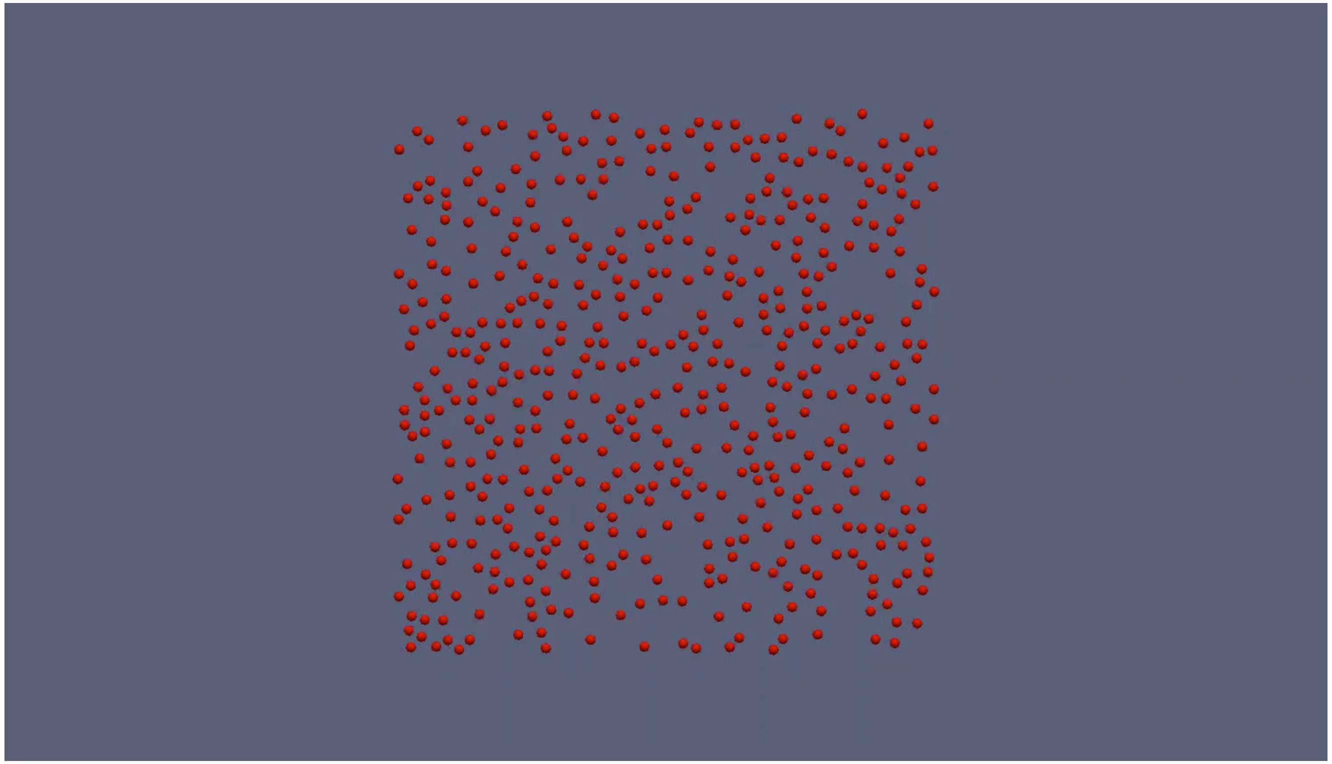
Density fluctuations

A proper indicator to distinguish dynamical regimes? $\sigma^2_{\mathcal{S}}(t) \equiv (1/N)\sum_{i=1}^{N}(\mathcal{S}_i - \overline{\mathcal{S}})^2$

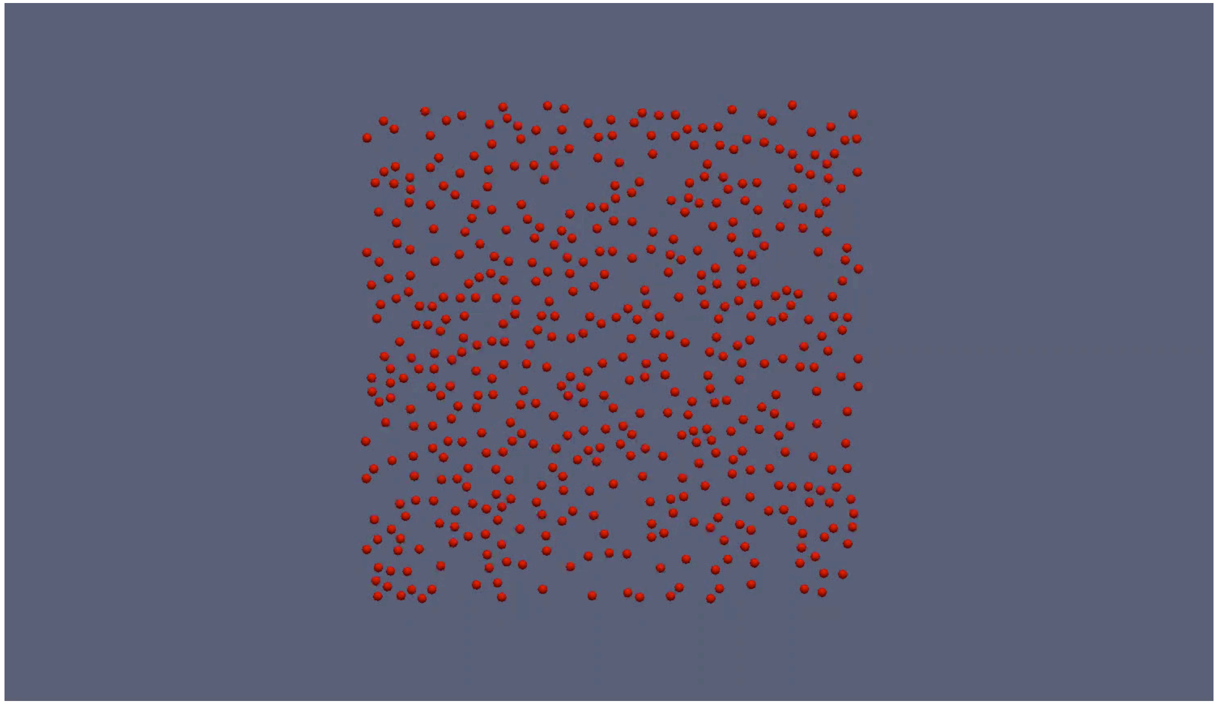
Use variance of Voronoi tesselation

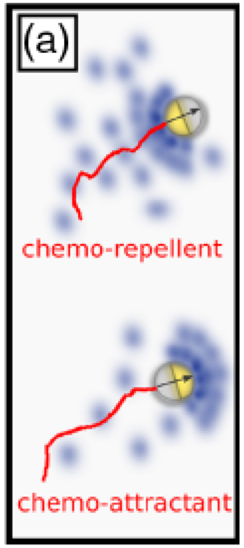


3. SELF-DIFFUSIOPHORETIC COLLOIDS



No hydrodynamics





Continuum model
Minimal symmetries / processes

$$\dot{\rho} = -\nabla \cdot (\rho v_0 \mathbf{p}) + D_\rho \nabla^2 \rho,$$

$$\dot{\mathbf{p}} = -\gamma \mathbf{p} + D_p \nabla^2 \mathbf{p} + \beta \nabla c - \gamma_2 |\mathbf{p}^2| \mathbf{p},$$

$$\dot{c} = D_c \nabla^2 c + k_0 \rho - k_d c + k_a \nabla \cdot (\rho \mathbf{p}).$$

basic ingredients

colloid concentration - propulsion

colloid orientation - self propulsion

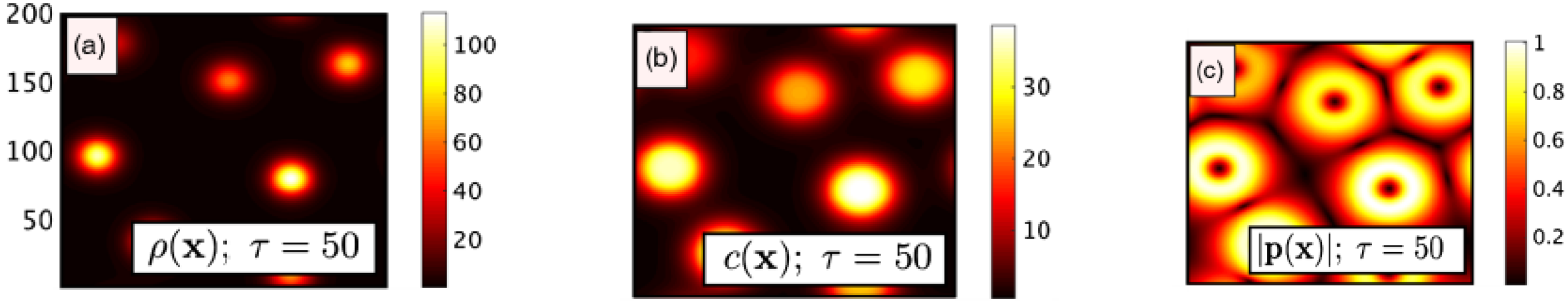
- chemoattractant/repellent

chemical concentration - production/degradation

-asymmetric production

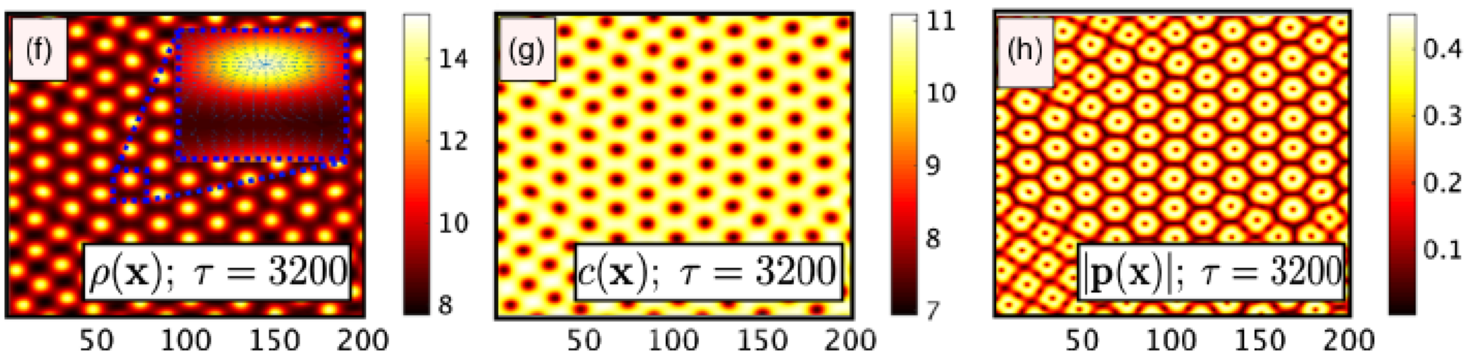
autophoresis

Chemoattractant



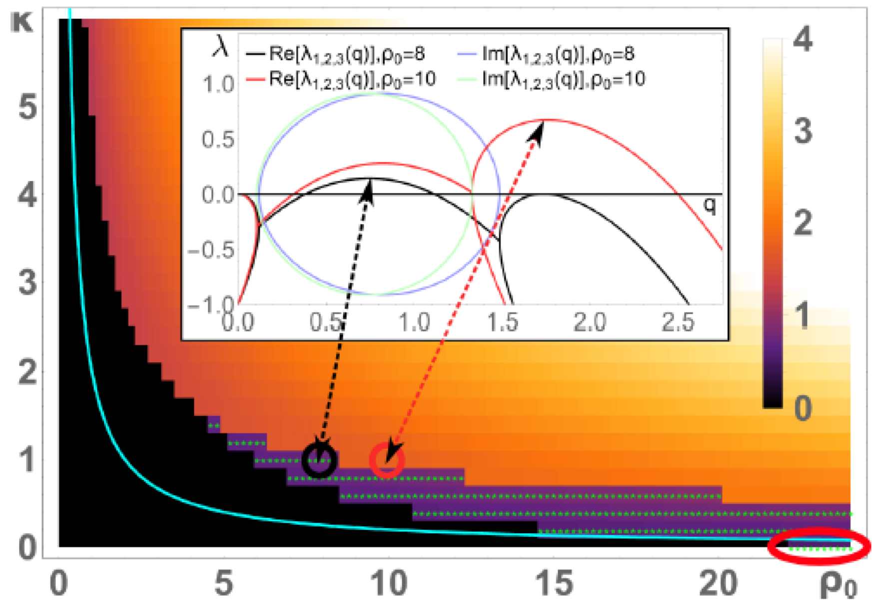
Colocalization colloid density / chemical concentration

Chemorepellant



Arrested growth

Quantify instability



Fast reorientation

$$\mathbf{p} = (s/\Gamma)\nabla c$$

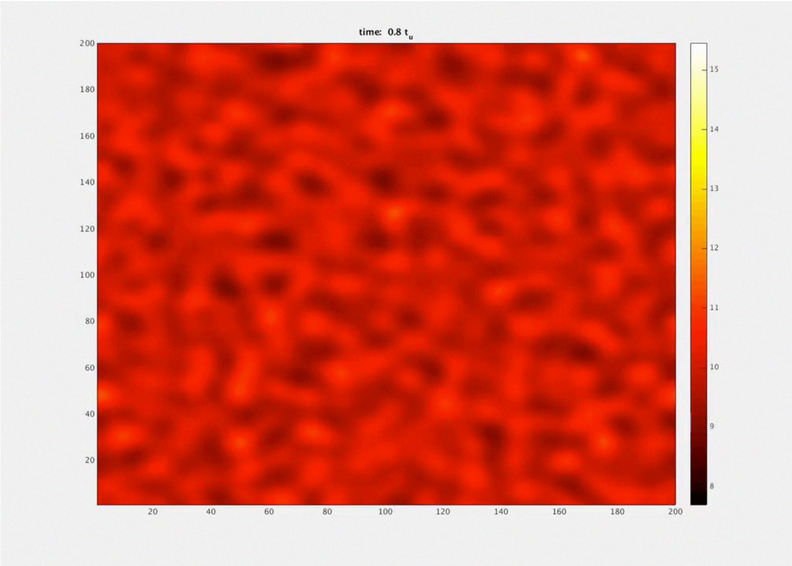
$$\dot{\rho} = -s\nabla\cdot(\rho\nabla c) + \nabla^2\rho,$$

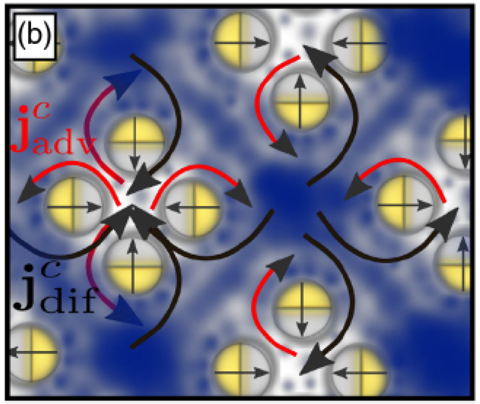
$$\dot{c} = s\kappa\nabla\cdot(\rho\nabla c) + \mathcal{D}_c\nabla^2 c + \rho - c$$

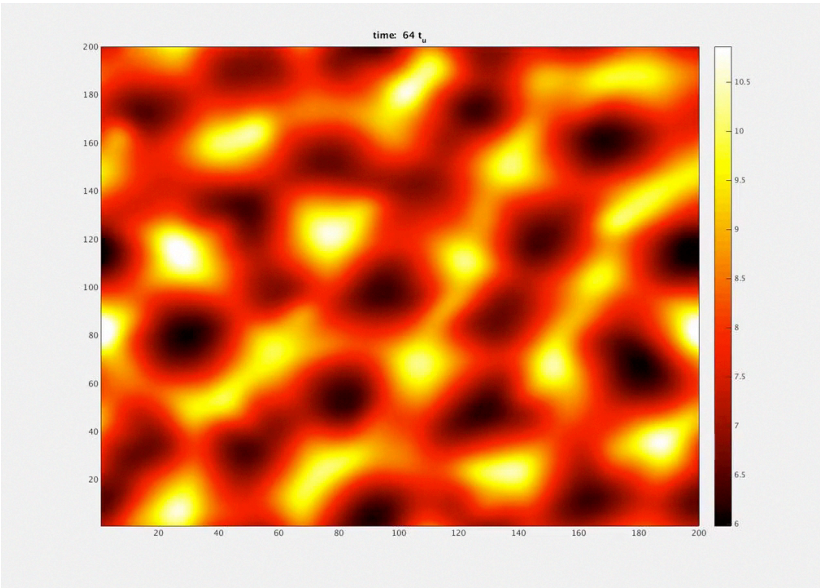
Janus instability
requires anisotropy

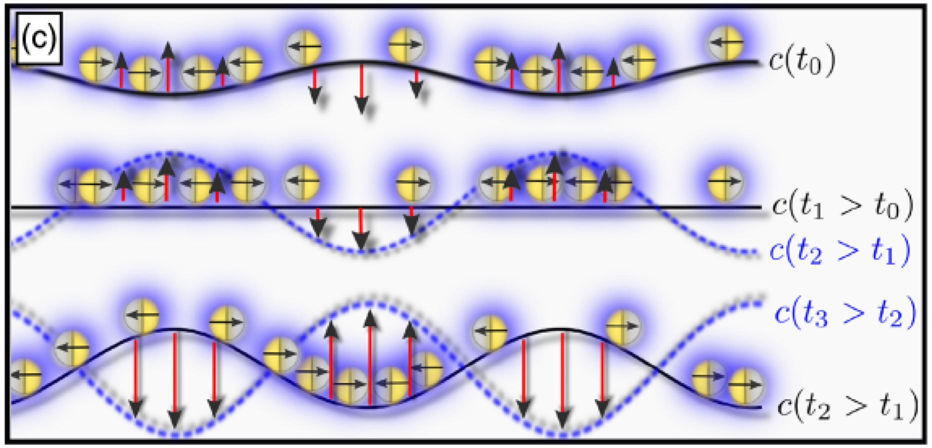
$$k_a\beta\rho_0 > \gamma D_c.$$

Slow reorientation
- Oscillatory instability
- Second instability mechanism


time: 0.8 t_u


(b)
$\mathbf{j}^c_{adv}$
$\mathbf{j}^c_{dif}$


time: 64 t_u


(c)
$c(t_0)$
$c(t_1 > t_0)$
$c(t_2 > t_1)$
$c(t_3 > t_2)$
$c(t_2 > t_1)$

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Intrinsically out of equilibrium moving particles
- Strong tendency to self organize
- Sensitive to environment changes

Magnetic colloids
- hydro/magnetic competition
- rich scenarios under confinement
  - variety of morphologies

Chemical swimmers
- competition hydrodynamic/chemical interactions

Phoretic mobility plays a relevant role
- (Non-eq) transition from crystal to clusters

Chemical signaling mainly determines clustering
- Hydrodynamics has a strong impact in kinetics
- Prevents gravitational collapse?

Competing mechanisms for dynamic clusters
- Hydrodynamics
- retardation in polarization

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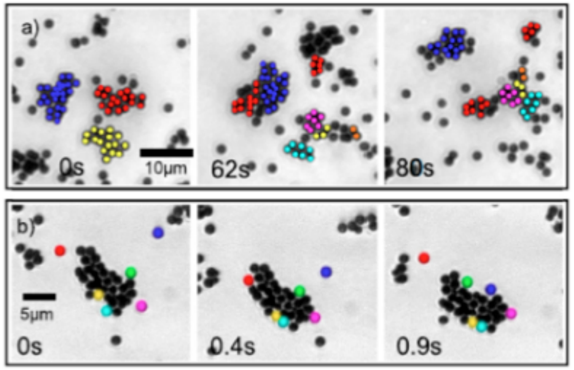
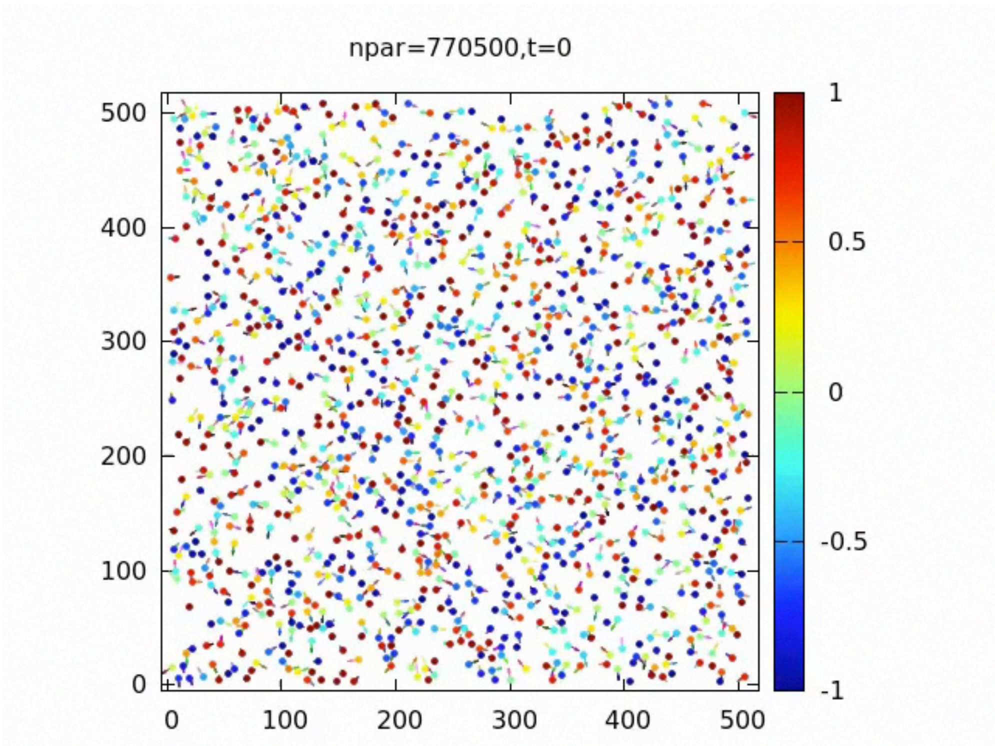
Mechanisms leading to dynamic rotating clusters



Clusters grow and coalesce
small mobility

Experimental evidence
more dynamic
clear rotation

Hydrodynamics + fixed directionality enough to promote rotating clusters

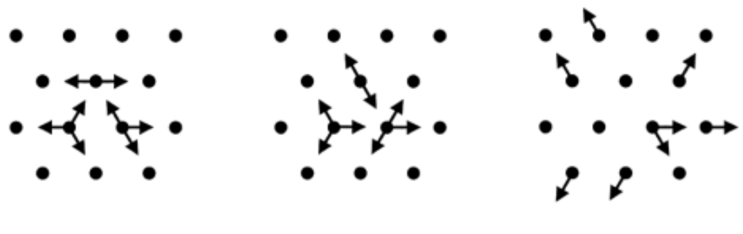


Fundamentals underlying cluster motion / rotation

more generic mechanisms?

2. Microswimmer suspension: Model

Lattice kinetic model: "microscopic" dynamics



$$f_i(r + c_i, t+1) = f_i(r,t) - \omega[f_i(r,t) - f_i^{eq}(r,t)]$$

$$\sum f_i = \rho$$

$$\sum f_i c_i = \rho v$$

$$\sum f_i c_i c_i = \rho vv + P$$

Conserved variables
Proper symmetries

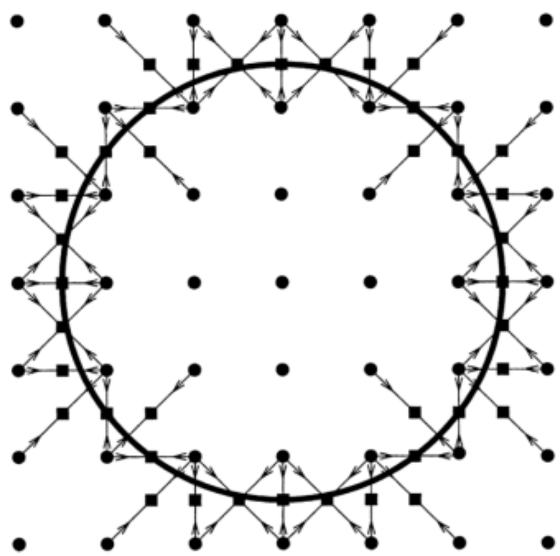
Hydrodynamic equations

Colloid

rigid hollow surface

collision

bounce-back

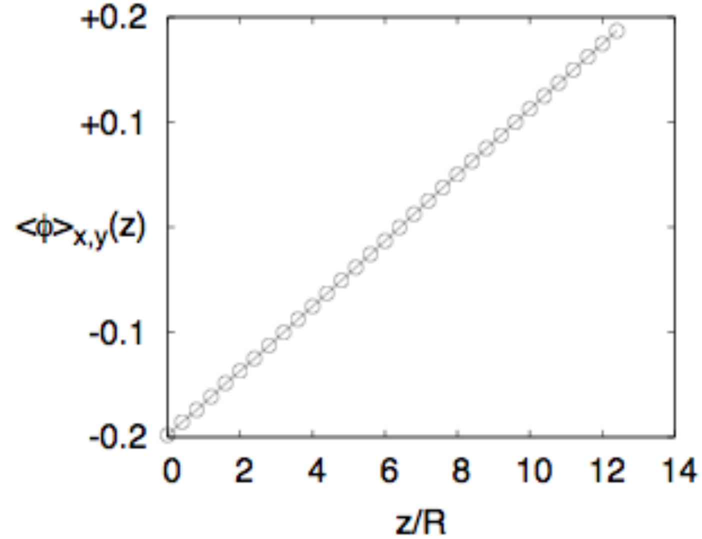


Hybrid scheme: molecular dynamics

Pre-selection of relevant degrees of freedom

3.Test case: chemotaxis

Directed motion of a colloidal particle
in a linear concentration profile $\phi(\mathbf{r}) = \phi_0 + \beta z$

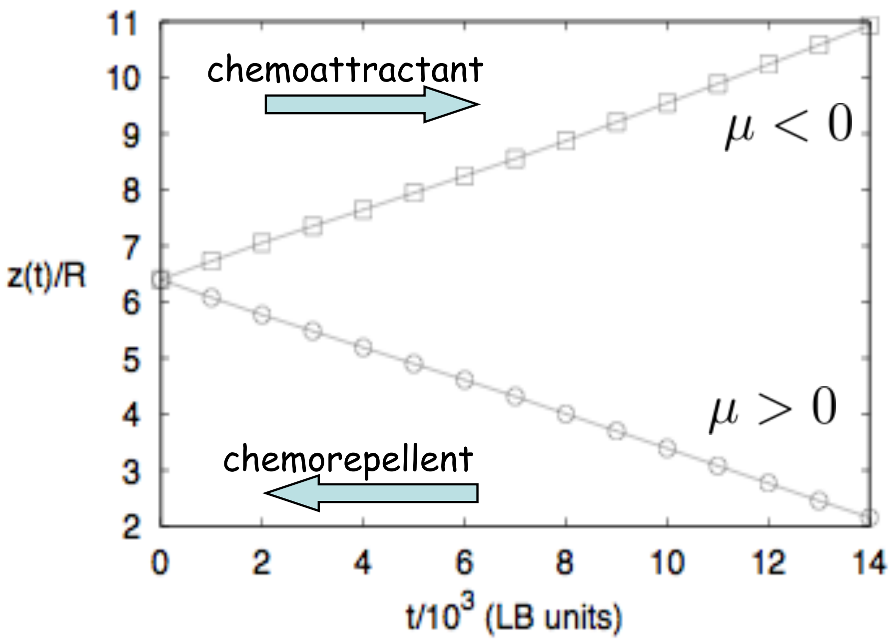


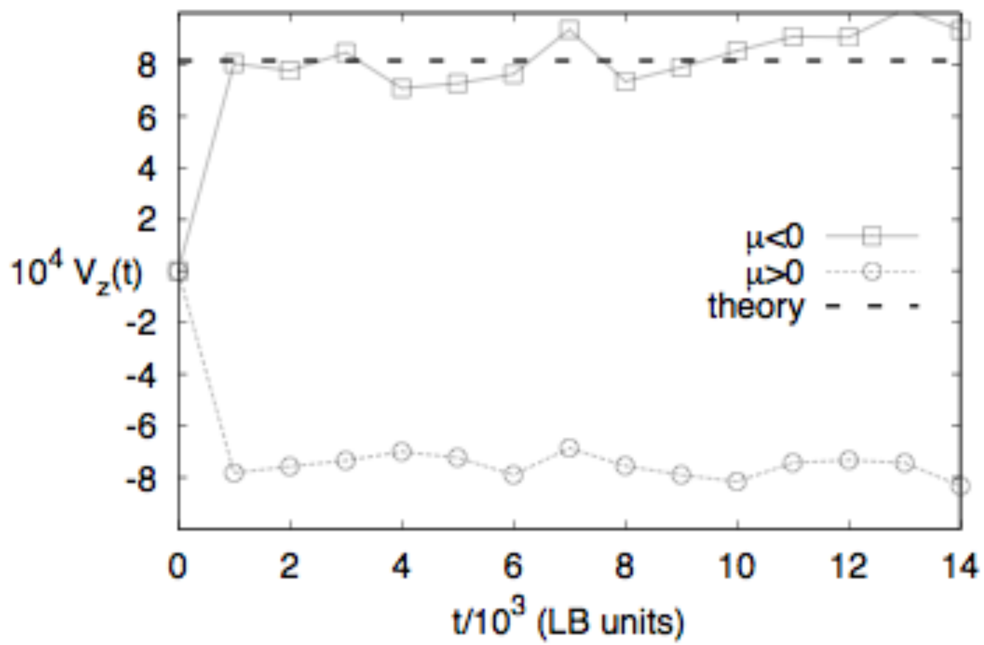
For constant mobility the propulsion velocity

$$\mathbf{V} = -\frac{1}{4\pi R^2}\int\int_{\Sigma}\mu(\mathbf{r}_S)(\mathbf{I}-\hat{n}\otimes\hat{n})\nabla\phi(\mathbf{r}_S)d\mathbf{r}_S$$

can be calculated exactly

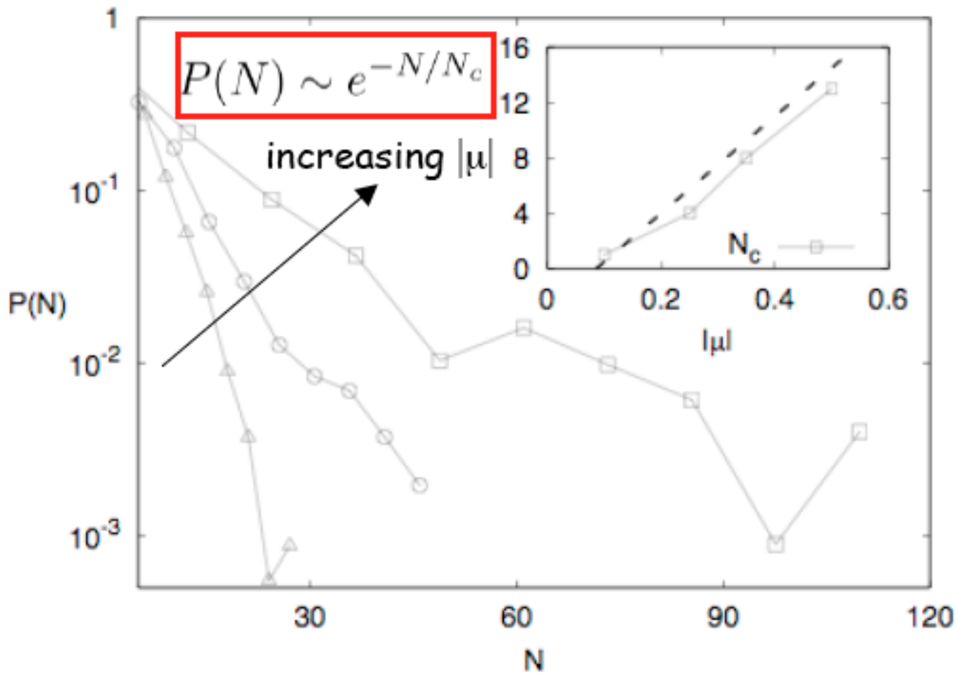
$$\mathbf{V} = -\frac{2}{3}\beta\mu\mathbf{e}_z$$





Statistics and geometry of clusters

PDF and mean particle number as function of coupling strength



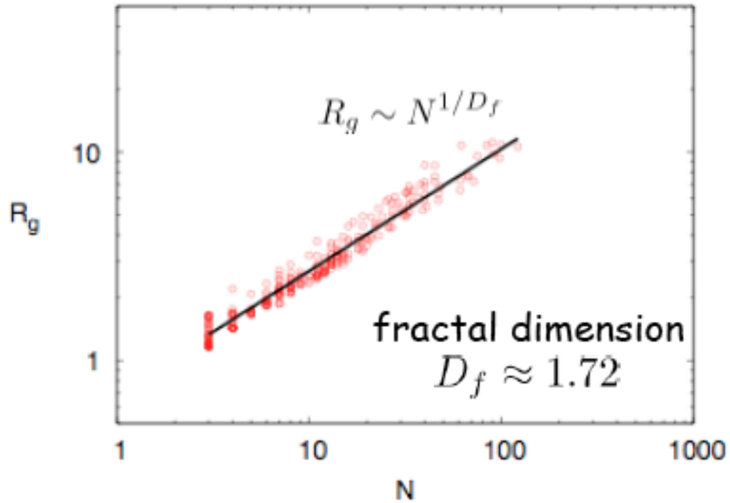
$\langle N \rangle \sim V_p$ ⇨ $N_c \sim \mu$

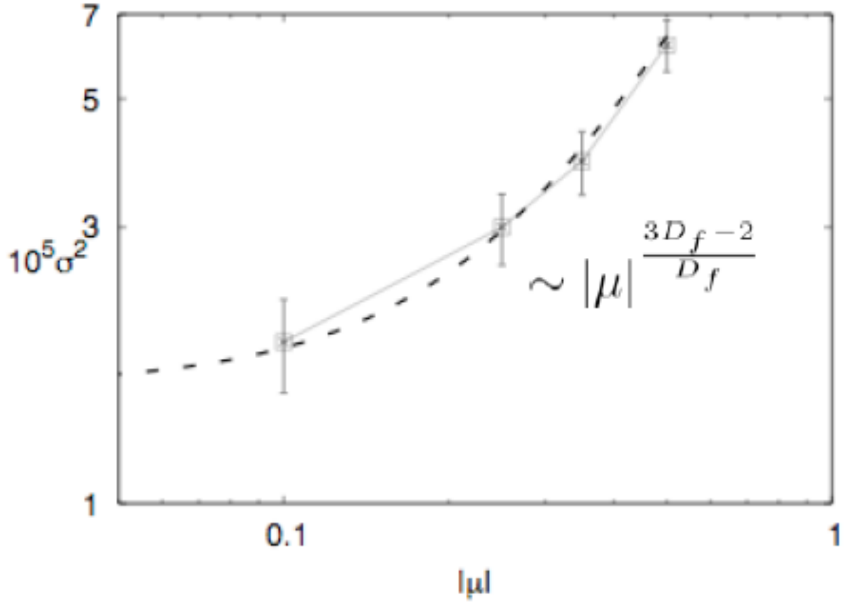
(Theurkauff et al)

colloids live on a set $\mathcal{S} = \bigcup_{i=1}^{N_{clus}} \mathcal{C}_i$ (i-th cluster)

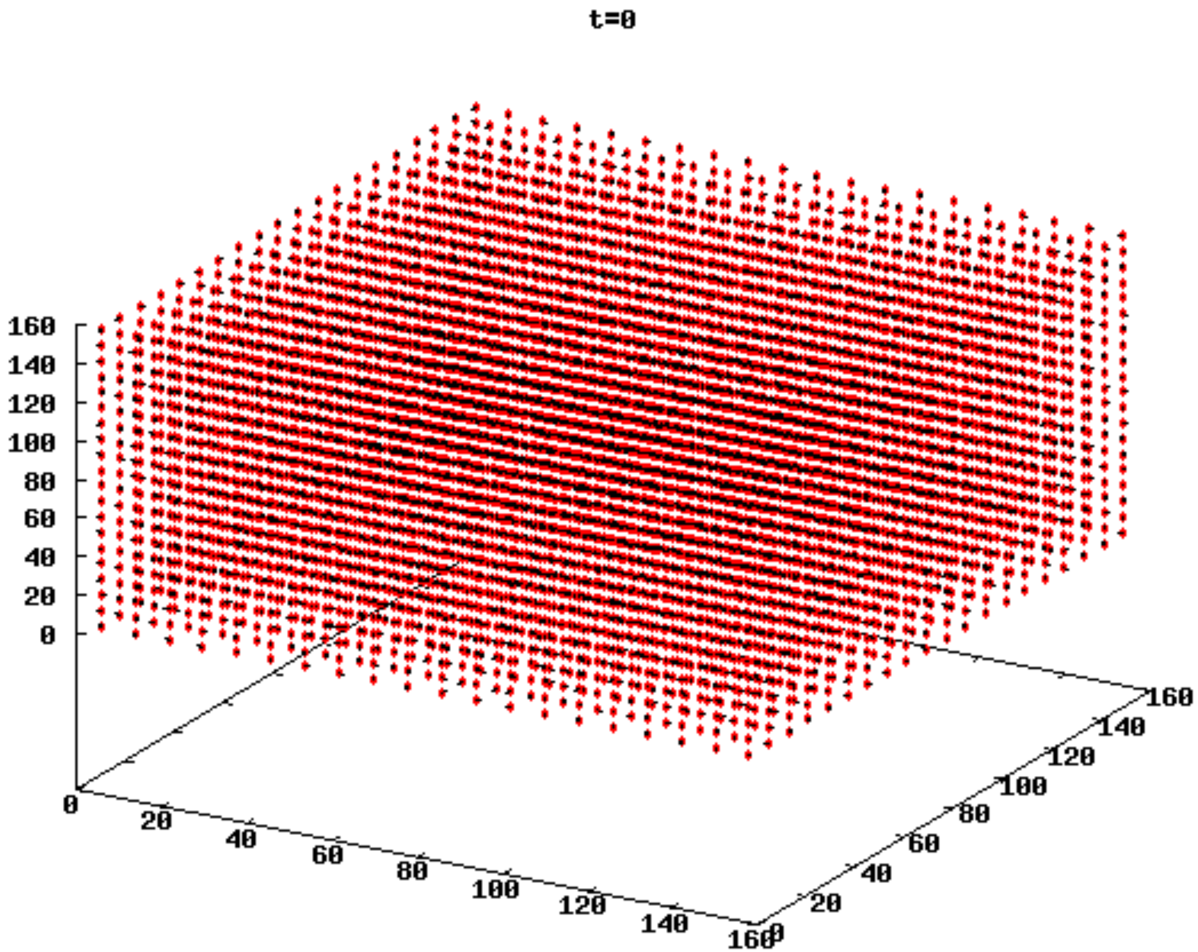
$$\sigma_\rho^2 \sim \langle \rho(x)^2 \rangle \propto \sum_{i=1}^{N_{clus}} \left(\frac{N_i}{\mathcal{A}_i} \right) \mathcal{A}_i P(\mathcal{A}_i) \sim \mu^{\frac{3D_f - 2}{D_f}}$$

gyration radius vs number of colloids





3. Self-phoretic swimmers in 3D



Large clusters

percolating

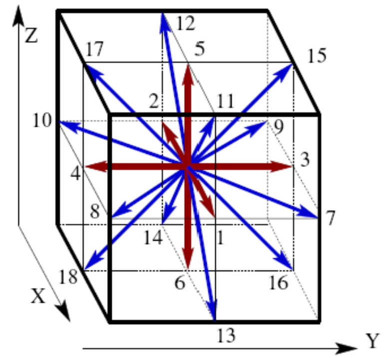
transient?

(Hybrid) Lattice Boltzmann algorithm for multiphase fluids + (resolved) particles

Solvent

$$f_l(\mathbf{x}+\mathbf{c}_l\Delta t, t+\Delta t) - f_l(\mathbf{x},t) = -\frac{\Delta t}{\tau}\left(f_l(\mathbf{x},t) - f_l^{(eq)}(\mathbf{x},t)\right)$$

$$\rho(\mathbf{x},t) = \sum_l f_l \qquad \rho(\mathbf{x},t)\mathbf{u}(\mathbf{x},t) = \sum_l \mathbf{c}_l f_l \qquad l = 0,\ldots,18$$



in the limits $Kn = \frac{\lambda_{mfp}}{L} \ll 1 \qquad Re_p = \frac{vR}{\nu} \ll 1 \qquad Ma = \frac{v}{c_s} \ll 1$

$$\rho(\partial_t \mathbf{v} + (\mathbf{v}\cdot\nabla)\mathbf{v}) = -\nabla p + \eta\nabla^2\mathbf{v} - \phi\nabla\mu$$

"Fuel"

$$\partial_t \phi + \mathbf{v}\cdot\boldsymbol{\nabla}\phi = M\nabla^2\mu$$

Advection-diffusion equation via finite differences

feedback on the fluid via a forcing term in the LB equilibria $\mathbf{F} \propto \phi\nabla\phi$

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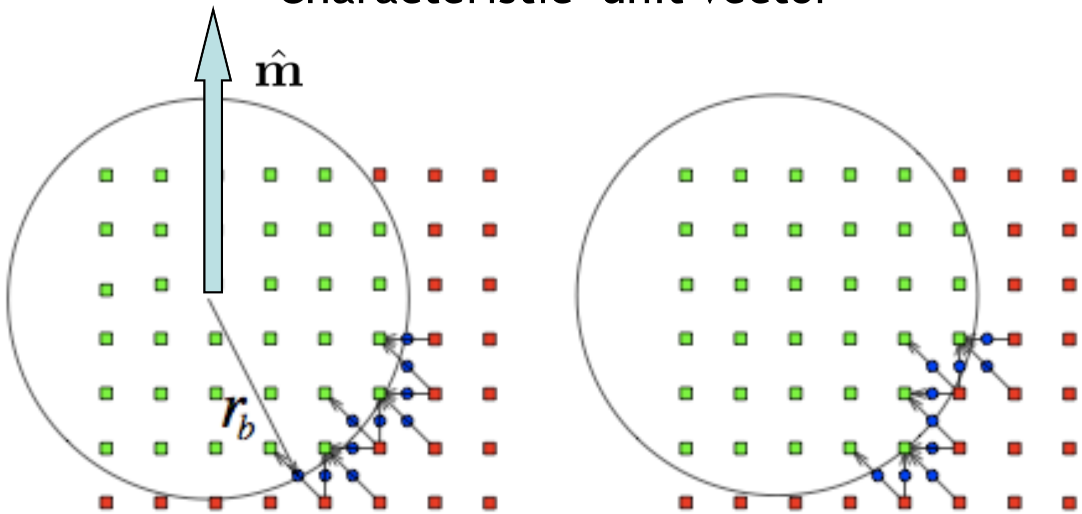
Lattice Boltzmann algorithm for multiphase fluids + (resolved) particles

Colloidal particles

Characteristic unit vector



(AJC Ladd, J. Fluid Mech. **271**, 285 (1994))

bounce-back-on-links algorithm: mass/momentum conservation between particle and fluid

$$f_{l'}(\mathbf{x}, t + \Delta t) = f_l^*(\mathbf{x}, t) - \frac{2a_{c_l}\rho \mathbf{u}_l \cdot \mathbf{c}_l}{c_s^2}$$

$$\mathbf{u}_l = \mathbf{U} + \mathbf{\Omega} \wedge (\mathbf{x}_l - \mathbf{X}_{CoM})$$

+ position dependent slip velocity at the particle surface

$$\mathbf{v}(\mathbf{r}_S) = \mu(\mathbf{r}_S)(\mathbf{I} - \hat{\mathbf{n}} \otimes \hat{\mathbf{n}})\nabla\phi(\mathbf{r}_S)$$

Pair velocities: Low Re

$$\mathbf{v}_a = \mathbf{G}^{(a)} \cdot \mathbf{F}^a + \mathbf{G}^{(a,b)} \cdot \mathbf{F}^b$$
$$\mathbf{v}_b = \mathbf{G}^{(a,b)} \cdot \mathbf{F}^a + \mathbf{G}^{(b)} \cdot \mathbf{F}^b$$

$$\mathbf{G}^{(a)} = C_{\|}^{(a)}(\mathbf{r}_a)(\mathbf{1} - \hat{z}\hat{z}) + C_{\perp}^{(a)}(\mathbf{r}_a)\hat{z}\hat{z}$$

Constraint: COM + orientation

linear relation

$$\mathbf{V} - \frac{2L}{1+\gamma^{-3}}\frac{d\mathbf{n}}{dt} = [\mathbf{G}^{(a,b)} - \mathbf{G}^{(a)}] \cdot (\mathbf{1} - \mathbf{nn}) \cdot \mathbf{F}$$
$$\mathbf{V} + \frac{2L}{1+\gamma^{3}}\frac{d\mathbf{n}}{dt} = [\mathbf{G}^{(b)} - \mathbf{G}^{(a,b)}] \cdot (\mathbf{1} - \mathbf{nn}) \cdot \mathbf{F}$$

$$\Rightarrow \quad \mathbf{V} = 2L\mathbf{N} \cdot \mathbf{M}^{-1} \cdot \frac{d\mathbf{n}}{dt}$$

Effective mobilities

$$\mathbf{M} \equiv \mathbf{G}^{(a)} + \mathbf{G}^{(b)} - 2\mathbf{G}^{(a,b)}$$
$$\mathbf{N} \equiv \frac{1}{1+\gamma^3}[\mathbf{G}^{(a,b)} - \mathbf{G}^{(a)}] + \frac{1}{1+\gamma^{-3}}[\mathbf{G}^{(b)} - \mathbf{G}^{(a,b)}]$$

Asymmetric particle/wall friction

$$\frac{d\mathbf{n}}{dt} = \boldsymbol{\omega} \times \mathbf{n}, \qquad \boldsymbol{\omega} = \frac{1}{\zeta_r}\mathbf{T} = \frac{\mu_0}{\zeta_r}\mathbf{m} \times \mathbf{H} = \frac{\mu_0 V_d H \chi}{\zeta_r}\mathbf{n} \times \mathbf{H}.$$

For circular trajectory:

$$\mathbf{n}(t) = (\sin\theta\sin(\Omega t + \varphi), \cos\theta, \sin\theta\cos(\Omega t + \varphi))$$

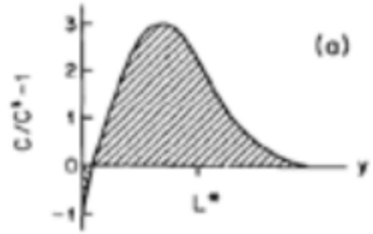
Net average velocity

$$< V_x > = \frac{9}{8}R_a\Omega\left[-1 + \frac{1}{\sqrt{1 - \frac{R_a^2}{h^2}\sin^2\theta}}\right]$$

Diffusioosmosis

concentration interacts with a solid surface

Delocalized membrane?



$$C = C^s \exp(-\Phi/kT),$$

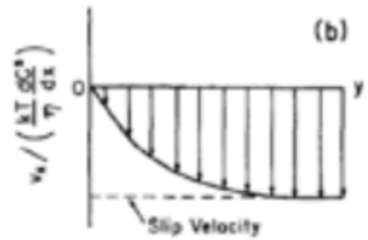
Equilibrium away from wall
equality of chemical potential

$$\frac{\partial p}{\partial y} + C\frac{d\Phi}{dy} = 0;$$

concentration gradient along surface

longitudinal pressure gradient

unbalanced ⇨ $$\eta \frac{\partial^2 v_x}{\partial y^2} - \frac{\partial p}{\partial x} = 0.$$



Surface-induced flow

Slip velocity

$$v^s = -\frac{kT}{\eta}\int_0^\infty y[\exp(-\Phi/kT) - 1]\, dy \frac{dC^s}{dx}$$