

Collective behaviour of chemotactic colloids: Clusters, Asters and Oscillations

Suropriya Saha², Ramin Golestanian³, Sriram Ramaswamy^{1,2}

¹ TIFR Centre for Interdisciplinary Sciences, Hyderabad

² Physics, IISc, Bangalore

³ Theory Physics, Oxford

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Motility

- Directed force-free motion
- Flocking
- Gradient-sensing
- Signalling
- Clumping
- Patterns

Can inanimate matter imitate this?

The Catalytic Colloid

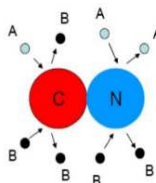
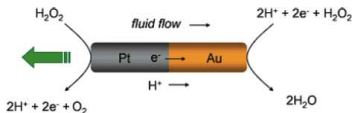


FIG. 1 (color online). Catalytic (C) and noncatalytic (N) dimer spheres and the collision events that occur on interaction of the A and B species with each sphere.

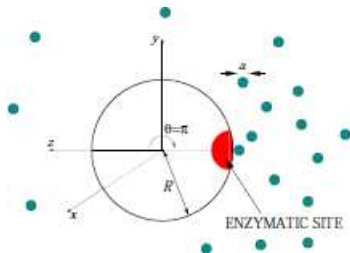


Figure : The eletrokinetic swimmer (Paxton et al 2005), the chemically powered nanodimers (Kapral et al. 2007) and The Ddfusiophoretic Swimmer (Golestanian et al. 2005).

The Plan of the talk

- Self-Diffusiophoresis
- Chemotaxis in an external gradient
- Single Particle motion in external reactant field
- Collective behaviour

Phoresis

- Extended object moves when placed in external gradient of 'something' that interacts with its surface.
- 'Something' can be
 - Electric potential - Electrophoresis
 - Chemical Species - Diffusiophoresis
- Force free motion
- Screening layer
- Colloids - $Re = 0$ → Stokes Regime.
- Colloid coated with catalysts and placed in substrate bath
- localised product gradients → self phoretic propulsion

Phoresis

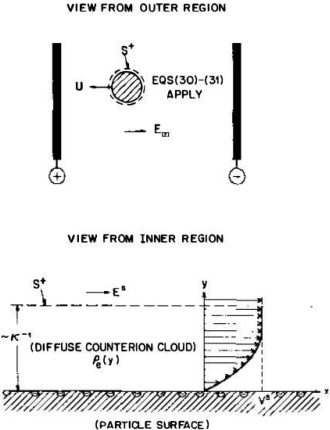
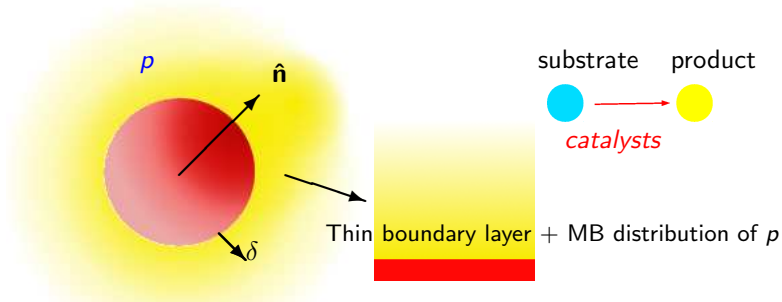


Figure 1 Electrophoresis of a charged particle. κ^{-1} is the Debye screening length of the solution, defined by (4). v^s is the “slip velocity,” which is given by (6) with ζ (taken to be negative here) equal to the electrostatic potential at $y = 0$. E^s is the electric field at the outer edge of the double layer (S^+).

Figure : Screening length, separation of ‘outer’ and ‘inner’ region; Anderson 1986.

Swimmer in a uniform substrate field

colloid coated in a pattern - $\sigma(\theta)$ - produces diffusion field p



Momentum balance

$$\frac{\partial \Pi}{\partial z} + p_b \frac{\partial \phi}{\partial z} = 0 \quad \longrightarrow$$

$$\eta \frac{\partial^2 v_x}{\partial z^2} - \frac{\partial \Pi}{\partial x} = 0$$

$$p(z) = p_b e^{\phi/k_B T}$$

ϕ - interaction potential

Slip velocity

$$v_s(\mathbf{r}) = \mu(\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}) \cdot \nabla p_b$$

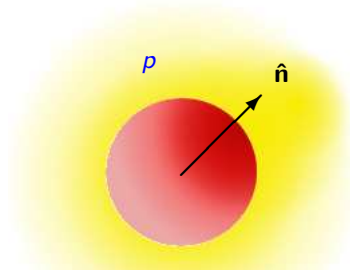
Mobility

$$\mu = \frac{k_B T}{\eta} \int_0^\infty z [e^{(-\frac{\phi}{k_B T})} - 1] dz$$

Anderson *et al.* 1989

Swimmer in a uniform substrate field

Golestanian *et al.* 2005



product diffuses $\partial_t p = D_p \nabla^2 p$

$$D_p \frac{\partial p}{\partial r} \Big|_a = \kappa \sigma(\hat{n})$$

Use p to get

$$\mathbf{V} = \frac{1}{4\pi} \int \mathbf{v}_s(\mathbf{r}) d\Omega$$
$$\omega = \frac{3}{16\pi R} \int \hat{\mathbf{r}} \times \mathbf{v}_s(\mathbf{r}) d\Omega$$

\mathbf{V} , ω obtained using

Force and Torque balance $\int_{\Sigma_\alpha} \hat{\mathbf{n}} \cdot \boldsymbol{\tau} d^2\mathbf{r}$, $\int_{\Sigma_\alpha} \mathbf{r} \times \boldsymbol{\tau} d^2\mathbf{r}$

Reciprocity theorem -

for solutions \mathbf{v}_1 , \mathbf{v}_2 to Stokes eq. for b.c. $\mathbf{u}_1 \Big|_{\Sigma_\alpha} = \mathbf{V} + \boldsymbol{\Omega} \times \mathbf{R}$

$\mathbf{u}_2 \Big|_{\Sigma_\alpha} = \mathbf{v}_s$, $\mathbf{u}_{1,2} \Big|_{r \rightarrow \infty} = 0$.

Keh *et al.* 1976

Colloid in an External Reactant Gradient

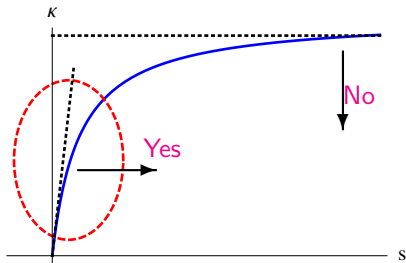
Let the substrate concentration vary spatially - $s(\mathbf{r})$

in a linear gradient - chemotaxis?

in a localised substrate profile - scattering / trapping?

Need rate κ to vary with s - typically **Michaelis-Menten** reaction kinetics.

$$\kappa(s) = \frac{\kappa_1 \kappa_2 s}{\kappa_2 + \kappa_1 s}$$



Calculation Details

s and p both diffuse $\partial_t p - D_p \nabla^2 p = 0$, $\partial_t s - D_s \nabla^2 s = 0$,

with B.Cs.

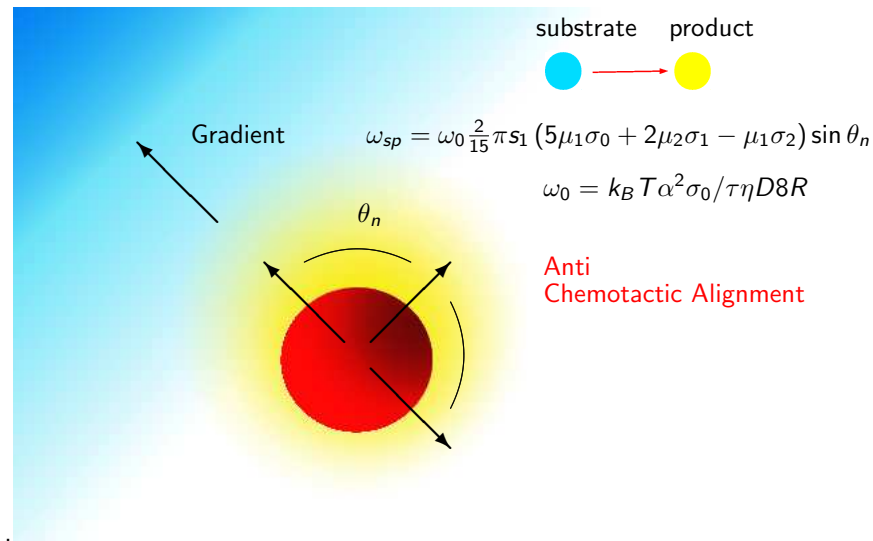
$$-D_s \hat{\mathbf{k}} \cdot \nabla s = -\kappa_1 s P_s \sigma(\theta, \phi), \quad -D_p \hat{\mathbf{k}} \cdot \nabla p = \kappa_2 P_p \sigma(\theta, \phi), \quad \kappa_2 P_p \equiv \kappa(s)$$

$\frac{D_p}{D_s} > 1$	$-\hat{\mathbf{k}} \cdot \nabla p _a = -\kappa_1 (s_b - \frac{D_p}{D_s} p) \sigma$ $s = (s_b - \frac{D_p}{D_s} p)$ Non linear dependence on colloid size	Limit not well defined	
$\frac{D_p}{D_s} = 1$			
$\frac{D_p}{D_s} < 1$	$-\hat{\mathbf{k}} \cdot \nabla p _a = \kappa_1 s_b \sigma$ $s = s_b$ Swimmer sensitive to gradients of s	$-\hat{\mathbf{k}} \cdot \nabla p _a = \kappa_2 \sigma$ $s = (s_b - \frac{D_p}{D_s} p)$ Swimmer insensitive to gradients of s .	
	$\kappa_1 s_0 / \kappa_2 < 1$	$\kappa_1 s_0 / \kappa_2 = 1$	$\kappa_1 s_0 / \kappa_2 > 1$

Details contd..

- Uniform substrate gradient along $\hat{\mathbf{z}}$
- Symmetry axis along $(\theta_n, \phi_n = 0)$.
- μ_p, σ expressed in spherical harmonics $\mu_{p\ell}, \sigma_\ell$ in the body fixed frame of swimmer
- Assume steady state $\partial_t p = 0$
- ω is now a function of θ_n through the B.C.

Swimmer in a linear gradient



Conditions for chemotaxis

- Single catalytic site insufficient; a finite coat of catalysts required.
- We can design the swimmer to be chemotactic or antichemotactic by suitable coating.
- If σ , μ_p contain odd or even harmonics alone - no propulsion - result holds for spheroids too.
- A sphere with uniform mobility does not chemotax.

Shape Dependence of ω

Uniform spheroidal caps of catalytic and mobility patterns as $\sigma(\theta) \propto \Theta(\theta - \alpha_1)$ and $\mu_p \propto 1 + \Theta(\theta - \alpha_2)$

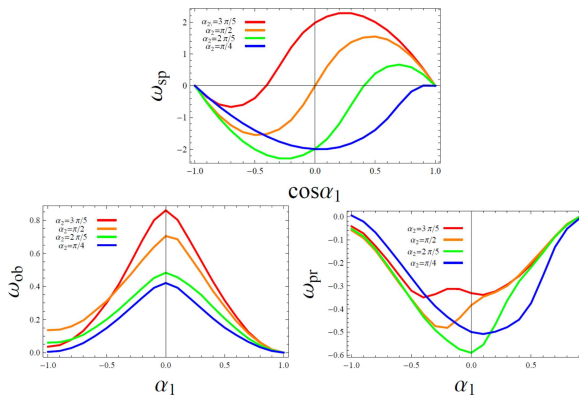


Figure : Angular velocities of colloids of various shapes (a) sphere (b) oblate (c) prolate as a function of α_1 at fixed values of α_2 .

Linear Velocity in a gradient

$\mathbf{V} = \mathbf{V}_p + \mathbf{V}_s$, with

$$\begin{aligned}\mathbf{V}_p &= -\frac{\kappa_1 s_0}{15D_p} (5\sigma_1\mu_{p0} + 2\sigma_2\mu_{p1} - \sigma_1\mu_{p2})\hat{\mathbf{n}} \\ &\quad - \frac{\kappa_1 s_1 R}{10D_p} \left(\sigma_0\mu_{p2} - \frac{2}{9}\sigma_1\mu_{p1} - 2\sigma_2\mu_{p0} + \frac{1}{35}\sigma_2\mu_{p2} \right) \hat{\mathbf{n}}\hat{\mathbf{n}} \cdot \hat{\mathbf{g}} \\ &\quad - \frac{\kappa_1 s_1 R}{30D_p} \left(10\sigma_0\mu_{p0} + \sigma_0\mu_{p2} + 2\sigma_1\mu_{p1} - 2\sigma_2\mu_{p0} + \frac{29}{35}\sigma_2\mu_{p2} \right) \hat{\mathbf{g}}, \\ \mathbf{V}_s &= -s_1 \left(\mu_{s0} + \frac{\mu_{s2}}{10} \right) \hat{\mathbf{g}} - \frac{\mu_{s2} s_1}{10} \mathbf{nn} \cdot \hat{\mathbf{g}}.\end{aligned}\tag{1}$$

Typical trajectories

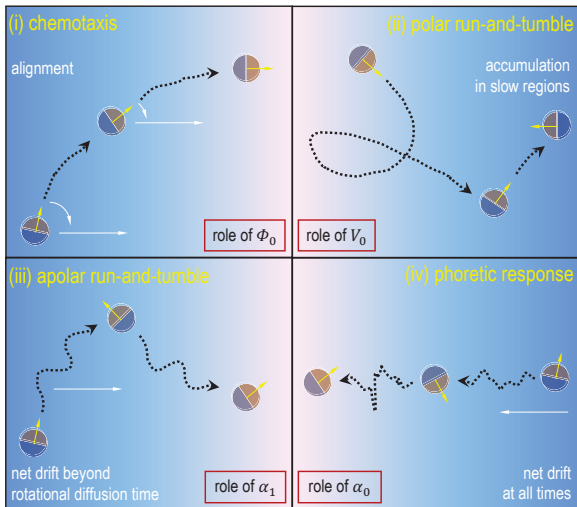


Figure : In each panel, three consecutive snapshots (with equal time intervals) are sketched together with typical connecting trajectories.

Collective behaviour

Consider a distribution $\rho(\mathbf{r}, t)$ of swimmers

S and P consumed and produced on surface of catalytic colloids resulting in fields $s(\mathbf{r}, t)$ and $p(\mathbf{r}, t)$.

Each swimmer responds to s through motility and chemotactic mechanisms.

The response of a swimmer to p is like that to any externally imposed solute gradient.

Hydrodynamic interactions ignored in this calculation.

Single Particle Dynamics

Langevin equations for the α th swimmer

$$\begin{aligned}\frac{d\mathbf{r}_\alpha}{dt} &= \overset{\text{Self Propulsion}}{V_0(s)\hat{\mathbf{n}}_\alpha} - \alpha_0 \nabla s - \alpha_1 \hat{\mathbf{n}}_\alpha \hat{\mathbf{n}}_\alpha \cdot \nabla s + \beta_0 \nabla p + \beta_1 \hat{\mathbf{n}}_\alpha \hat{\mathbf{n}}_\alpha \cdot \nabla p \\ &\quad + \sqrt{2D_r} \mathbf{f}_r(t), \\ \frac{d\mathbf{n}_\alpha}{dt} &= \Phi_0 (\hat{\mathbf{n}}_\alpha \times \nabla s) \times \hat{\mathbf{n}}_\alpha + \Omega_0 (\hat{\mathbf{n}}_\alpha \times \nabla p) \times \hat{\mathbf{n}}_\alpha \\ &\quad + \sqrt{2D_r} \hat{\mathbf{n}}_\alpha \times \mathbf{f}_n(t),\end{aligned}\tag{2}$$

Note: In the original image, arrows point from the text labels to the corresponding terms in the equations above.

where

$\Phi_0 > 0$ & $\Omega_0 > 0 \rightarrow$ chemotactic response to ∇s and ∇p

$\alpha_0 > 0$ & $\beta_0 > 0 \rightarrow$ attractive contributions to interactions due to s and p respectively

S and P consumed and generated at a rate

$$Q(\mathbf{r}, t) = \kappa(s) \sum_{\alpha} \int_{|\mathbf{x}_{\alpha}|=R} \delta(\mathbf{r} - \mathbf{r}_{\alpha} - \mathbf{X}_{\alpha}) \sigma(\mathbf{X}_{\alpha} \cdot \hat{\mathbf{n}}_{\alpha}), \quad (3)$$

\mathbf{X}_{α} = enzyme site on swimmer

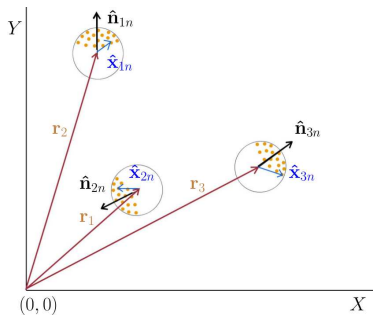


Figure : Schematic for the calculation of Q .

Develop Q to leading orders in ∇

Defining $\sum_{\alpha} \delta(\mathbf{r} - \mathbf{r}_{\alpha}) = \rho(\mathbf{r})$, $\sum_{\alpha} \hat{\mathbf{n}}_{\alpha} \delta(\mathbf{r} - \mathbf{r}_{\alpha}) = \mathbf{n}(\mathbf{r})$ to get

$$\begin{aligned} \text{Pe} \frac{D_p}{D_s} \frac{\partial s}{\partial t} - \nabla^2 s &= -K(s)(\rho - \epsilon \nabla \cdot \mathbf{n}), \\ \text{Pe} \frac{\partial p}{\partial t} - \nabla^2 p &= \frac{D_s}{D_p} K(s)(\rho - \epsilon \nabla \cdot \mathbf{n}). \end{aligned}$$

Péclet number $\text{Pe} \equiv Rv/D_p$, $K(s) = \kappa(s)NR^2/D_s$, $N = 4\pi R^2\sigma_0$ total enzymatic sites on swimmer and $\epsilon = \sigma_1/3\sigma_0$.

Let $Pe = 0$; linearise about ρ_0, s_0

$$\begin{aligned} s_q &= -\frac{K(s_0)}{q^2 + \xi_s^{-2}}(\rho_q - \epsilon\Theta_q) \\ \rho_q &= \frac{K(s_0)D_s/D_p}{(q^2 + \xi_s^{-2})}(\rho_q - \epsilon\Theta_q) \end{aligned} \quad (4)$$

$\xi_s = [\rho_0 K'(s_0)]^{-1/2}$ is nondimensional interaction range

$\xi_s \neq 0$ in linear part of MM

Here s eaten at lower rate than in the saturated part - long range nature suppressed

Call the ξ_s finite limit, the **unsaturated** case and $\xi_s \rightarrow \infty$, the **saturated**.

Equations of Motion

- Starting from the Langevin eq. EOM for the density ρ and \mathbf{n} constructed.
- Closure used: $\partial_t \mathbf{Q} = 0$, \mathbf{Q} slaved to \mathbf{n} and higher moments neglected
- S and P fields produced by inhomogeneities in ρ and divergence of \mathbf{n} mediate interactions between swimmers.
- The linearized dynamics in the isotropic phase closes in terms ρ and $\mathbf{n}_{Lq} = \hat{\mathbf{q}}\hat{\mathbf{q}} \cdot \mathbf{n}$.
- Coarse-grained equations presented in saturated limit and for wavenumbers $q \ll \xi_s^{-1}$ in unsaturated case.

Contrast to Flocking models

- Long ranged interactions.
- Interactions do not promote a global parallel alignment of \mathbf{n} .
- General tendency to form asters.
- A very different set of non-linearities from Toner-Tu.

Unsaturated

In the unsaturated case $\xi_s < \infty$, for wavenumbers $q \ll \xi_s^{-1}$, coarse grained equations read

$$\begin{aligned} & [\partial_t + 2D_r - (D + \frac{v_1^2 s_0^2}{30D_r})\nabla^2 + (\epsilon\rho_0\xi_s^2 A - \frac{v_1^2 s_0^2}{90D_r})\nabla\nabla\cdot]\mathbf{n}_L \\ & + \frac{(v_1 s_0 - \rho_0\xi_s^2 A)}{3\rho_0}\nabla\rho = 0, \\ & [\partial_t - (D - \rho_0\xi_s^2 B)\nabla^2]\rho_0^{-1}\delta\rho + (v_1 s_0 - \epsilon\rho_0\xi_s^2 B\nabla^2)\nabla\cdot\mathbf{n}_L = 0, \end{aligned} \tag{5}$$

where we define

$$\begin{aligned} A &= N\kappa(s_0) \left[\frac{\Omega_0}{D_p} - \frac{\Phi_0}{D_s} + \frac{V_0(s_0)}{2D_s} \frac{d \ln \kappa}{ds} \Big|_{s_0} \right], \\ B &= N\kappa(s_0) \left[\frac{1}{D_p} (\beta_0 + \frac{\beta_1}{3}) + \frac{1}{D_s} (\alpha_0 + \frac{\alpha_1}{3}) \right], \end{aligned} \tag{6}$$

Stability analysis

- In the overdamped limit, the unstable mode

$$-i\omega = -D'q^2 \equiv -\left(D + \frac{v_1^2 s_0^2}{6D_r} - \rho_0 \xi_s^2 B - \frac{v_1 s_0 \rho_0 \xi_s^2 A}{6D_r}\right)q^2, \quad (7)$$

goes unstable with growth rate $\sim q^2$ at small q .

- Competition with stabilizing effects at larger q will lead to a modulated growth morphology with a length scale $\sim |D'|^{1/2}$.
- Other mode, controlled by D_r , remains stable for $q \rightarrow 0$, i.e., interactions do not promote flocking.

Stability Analysis

On the stable side, the steady-state static small- q structure factor

$$S_\rho \propto \frac{1}{(D' + \gamma q^2)}, \quad (8)$$

where

$$\begin{aligned} \gamma = & 2\xi_s^2 D_r [\rho_0 \xi_s^2 B + \frac{\rho_0 \xi_s^2 A v_1 s_0}{6D_r} + \frac{1}{3} \epsilon \rho_0 \xi_s^2 B (v_1 s_0 - \rho_0 \xi_s^2 A) \\ & + (D - \epsilon \rho_0 \xi_s^2 A) (D + \frac{2v_1^2 s_0^2}{45D_r} - \rho_0 \xi_s^2 B) \\ & + D' (\rho_0 \xi_s^2 B + \epsilon \rho_0 \xi_s^2 A - 2D)]. \end{aligned} \quad (9)$$

For $\gamma > 0$, as $D' \rightarrow 0^+$, S_ρ displays fluctuations with a correlation length $\sqrt{\gamma/D'}$ that diverges as $D' \rightarrow 0 \rightarrow$ Clumping.

With $\gamma < 0$, the system has a tendency towards patterning with a characteristic length scale $\sim |\gamma|^{-1/2}$, implying a competition between the chemotactic (A) and phoretic (B) response to gradients.

Phase Diagram - Unsaturated

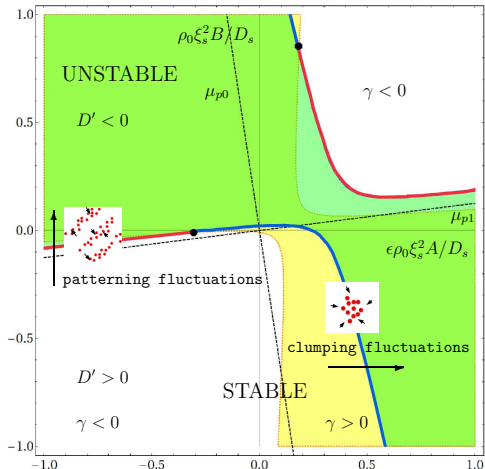


Figure : The phase diagram in the reaction-limited regime of abundant fuel shows a variety of possible states in the parameter space spanned by the effective rotational diffusivity D_r and effective interactions G . Possible experimental paths are shown as the two dashed lines. These could be explored in sequences of experiments on particles designed with suitable mobility coats.

Saturated

Define

$$\mathbf{E}(\mathbf{r}) = -\nabla \int_{\mathbf{r}'} \rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|, \quad (10)$$

The coarse grained equations are

$$\begin{aligned} & [\partial_t - (D + \frac{v_0^2}{30D_r})\nabla^2]\mathbf{n}_L + \frac{v_0}{3\rho_0}\nabla\rho + \frac{A}{3}\mathbf{E} \\ & - [\frac{v_0^2}{90D_r} - \frac{2\epsilon N\kappa_2 v_0 \rho_0}{135D_r}(\frac{\beta_1}{D_p} + \frac{\alpha_1}{D_s})]\nabla\nabla \cdot \mathbf{n}_L \\ & + [\frac{2\epsilon^2 A^2 \rho_0^2}{15D_r}n_L^2 - \frac{\epsilon A}{3}\rho_0 + 2D_r]\mathbf{n}_L = 0, \end{aligned} \quad (11)$$

$$(\partial_t - D\nabla^2)\rho + \rho_0(v_0 + \epsilon\rho_0 B)\nabla \cdot \mathbf{n}_L - \rho_0 B\nabla \cdot \mathbf{E} = 0, \quad (12)$$

Saturated - Stability Analysis

In the overdamped limit, i.e. for sufficiently large D_r , the relaxation rates of the eigenmodes are

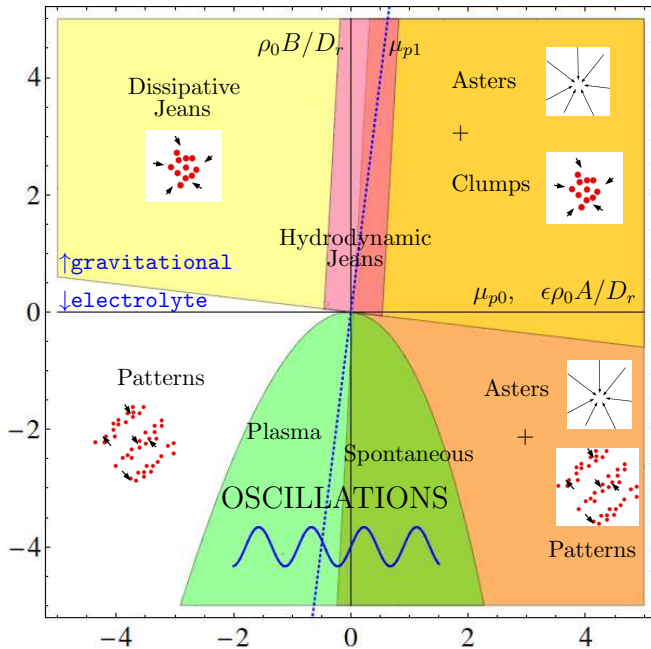
$$-i\omega = \begin{cases} \frac{G}{2D'_r} - [2D + \frac{v_0(v_0 + \epsilon\rho_0 B)}{3D'_r}]q^2, \\ -2D'_r + O(q^2), \end{cases}$$

where , $D_{eff} = D + \frac{v_0 v'_0}{6D'_r}$. (13)

where

- $D'_r = D_r - \epsilon\rho_0 A/6$ represents a modified rotational diffusion.
- $G = 2\rho_0 B D_r + \frac{1}{3}\rho_0 A v_0$ is an effective control parameter for the nature of interaction between the swimmers.

Saturated - Phase Diagram



Summary

- We have studied the dynamics of the catalytic colloid in a reactant gradient and categorized the different gradient seeking mechanisms.
- In particular we have shown that the chemotaxis can be controlled by changing mobility, catalytic coat and shape of the colloid.
- We have obtained the coarse grained equations for the density and polar order parameter of the colloids interacting via long ranged diffusion fields.
- The interplay of chemotaxis and phoresis leads to clumping and patterning at low reactant concentration; at high concentration, the slow decay of diffusing reactants and products yields analogues of electrostatic and gravitational phenomena Debye screening, microphase separation, plasma oscillations and gravitational collapse.