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MAX PLANCK SCHOOL matter to life

MAX-PLANCK-GESELLSCHAFT

Recent developments in chemically active matter I

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► **Three Topics:**

(I) Exact phoretic interaction of two chemically-active particles (with Babak Nasouri)

(II) Active phase separation in chemically active systems (with Jaime Agudo-Canalejo)

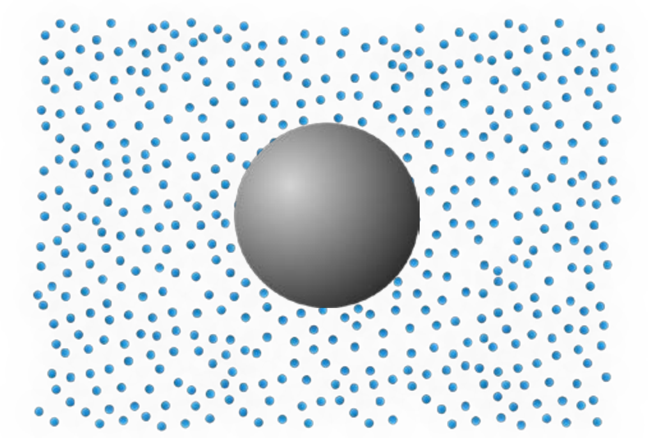
(III) Cooperatively enhanced reactivity and `stabilitaxis' of dissociating oligomeric proteins (with Jaime Agudo-Canalejo and Pierre Illien)

Exact phoretic interaction of two chemically-active particles

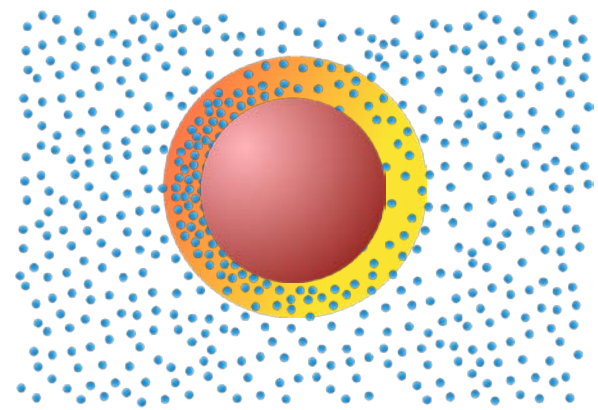
B. Nasouri & R. Golestanian, arXiv:2001.07576

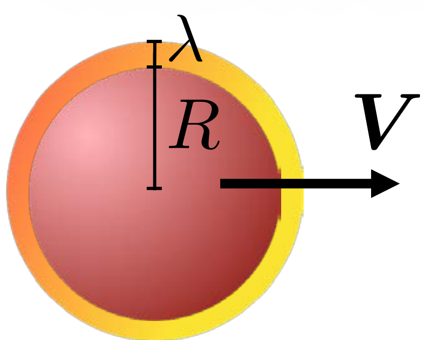
Chemically-active particles

passive



active

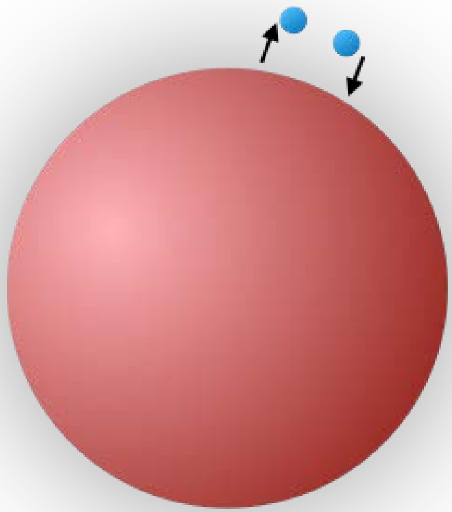




$$\boldsymbol{V} = -\frac{1}{A}\langle \boldsymbol{v}^{\mathrm{s}} \rangle$$

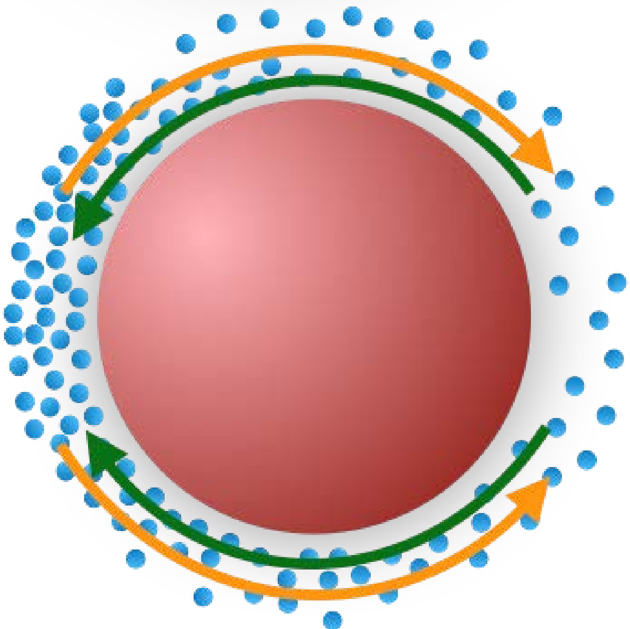
- If $\lambda/R \ll 1$, surface activity can be captured by local slip velocity ($\boldsymbol{v}^{\mathrm{s}}$)

Activity and Mobility



Chemical Activity (α):

- Characterizes how it produces or consumes chemicals



Chemical Mobility (μ):

- Characterizes how it responds to a chemical gradient

The continuum framework

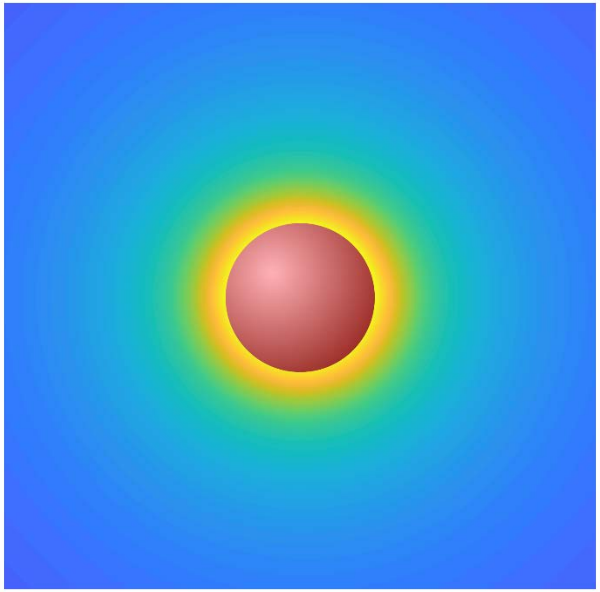
Overdamped regime:

- No fluid inertia (zero Reynolds number)
- No chemical advection (zero Pèclet number)

Single particle:

- Purely isotropic concentration gradient
- No propulsion

$$\boldsymbol{V} = \boldsymbol{0}$$



Pair interactions

Chemical interactions:

Hydrodynamic interactions:

Diffusion Equation

Stokes Equations

Slip Velocities

Pair interactions

Chemical interactions:

$$\nabla^2 C = 0$$

B.C. $$\begin{cases} -D\boldsymbol{n}_1 \cdot \boldsymbol{\nabla} C|_{\mathcal{S}_1} = \alpha_1 \\ -D\boldsymbol{n}_2 \cdot \boldsymbol{\nabla} C|_{\mathcal{S}_2} = \alpha_2 \end{cases}$$

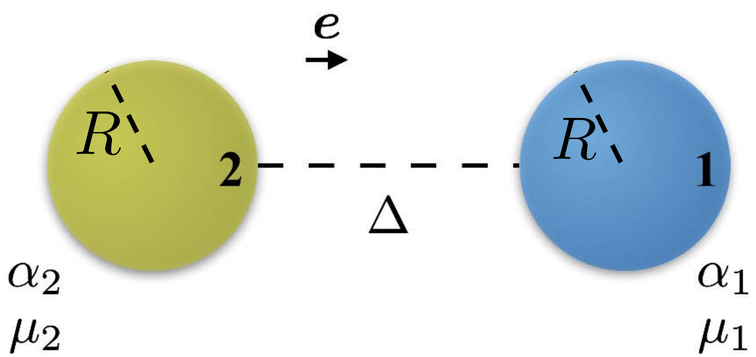
Hydrodynamic interactions:

$$\eta \nabla^2 \boldsymbol{v} = \boldsymbol{\nabla} p$$
$$\boldsymbol{\nabla} \cdot \boldsymbol{v} = 0$$

B.C. $$\begin{cases} \boldsymbol{v}|_{\mathcal{S}_1} = \boldsymbol{V}_1 + \boldsymbol{v}_1^{\mathrm{s}} \\ \boldsymbol{v}|_{\mathcal{S}_2} = \boldsymbol{V}_2 + \boldsymbol{v}_2^{\mathrm{s}} \end{cases}$$

$$\boldsymbol{v}_1^{\mathrm{s}} = \mu_1 \left(\boldsymbol{I} - \boldsymbol{n}_1\boldsymbol{n}_1\right) \cdot \boldsymbol{\nabla} C$$
$$\boldsymbol{v}_2^{\mathrm{s}} = \mu_2 \left(\boldsymbol{I} - \boldsymbol{n}_2\boldsymbol{n}_2\right) \cdot \boldsymbol{\nabla} C$$

'Far-field' solution

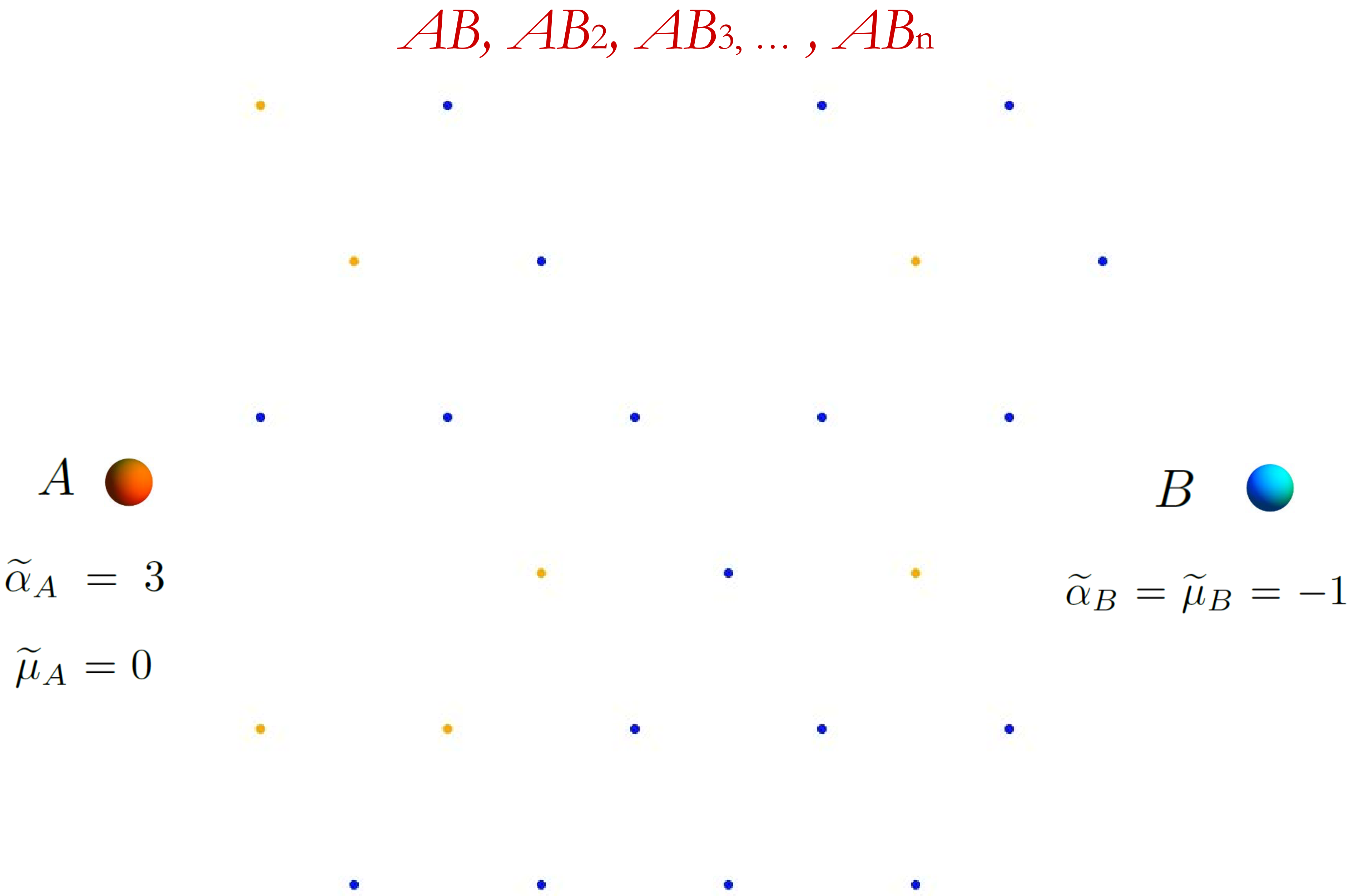


Assumptions:

- Large gap sizes ($\Delta/R \gg 1$)
- No hydrodynamic interactions
- No near-field chemical interactions

$$\boldsymbol{V}_1 = \frac{R^2 \boldsymbol{e}}{D\left(\Delta + 2R\right)^2} \alpha_2 \mu_1 \qquad \boldsymbol{V}_2 = \frac{-R^2 \boldsymbol{e}}{D\left(\Delta + 2R\right)^2} \alpha_1 \mu_2$$

R. Soto & R. Golestanian (2014)

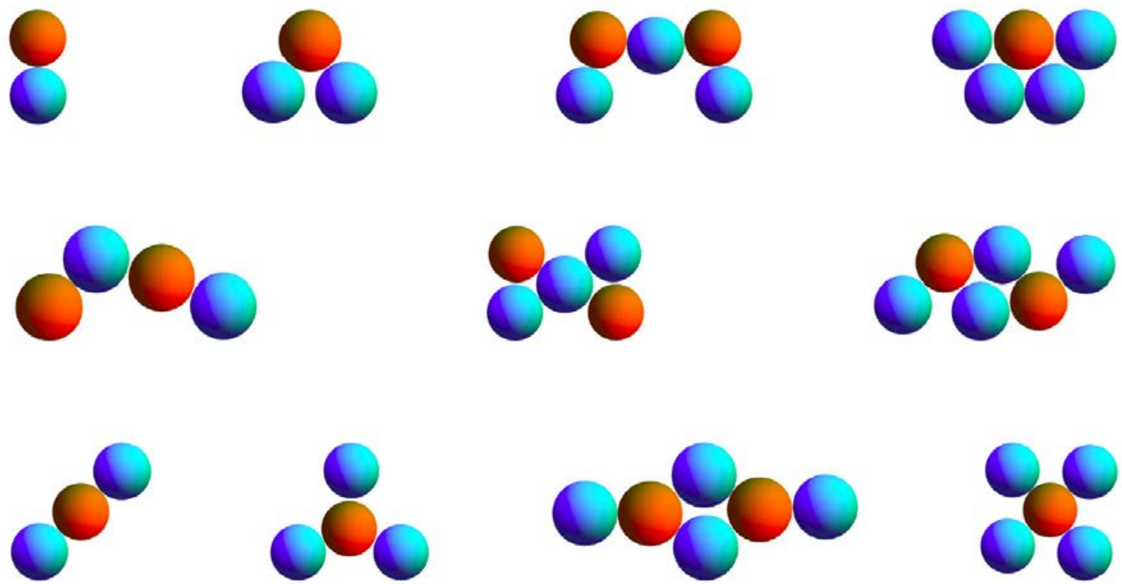

AB, AB2, AB3, ... , ABn
A
$\widetilde{\alpha}_A = 3$
$\widetilde{\mu}_A = 0$
B
$\widetilde{\alpha}_B = \widetilde{\mu}_B = -1$

Tabulating Active Molecules

Translational propulsion

Rotational propulsion

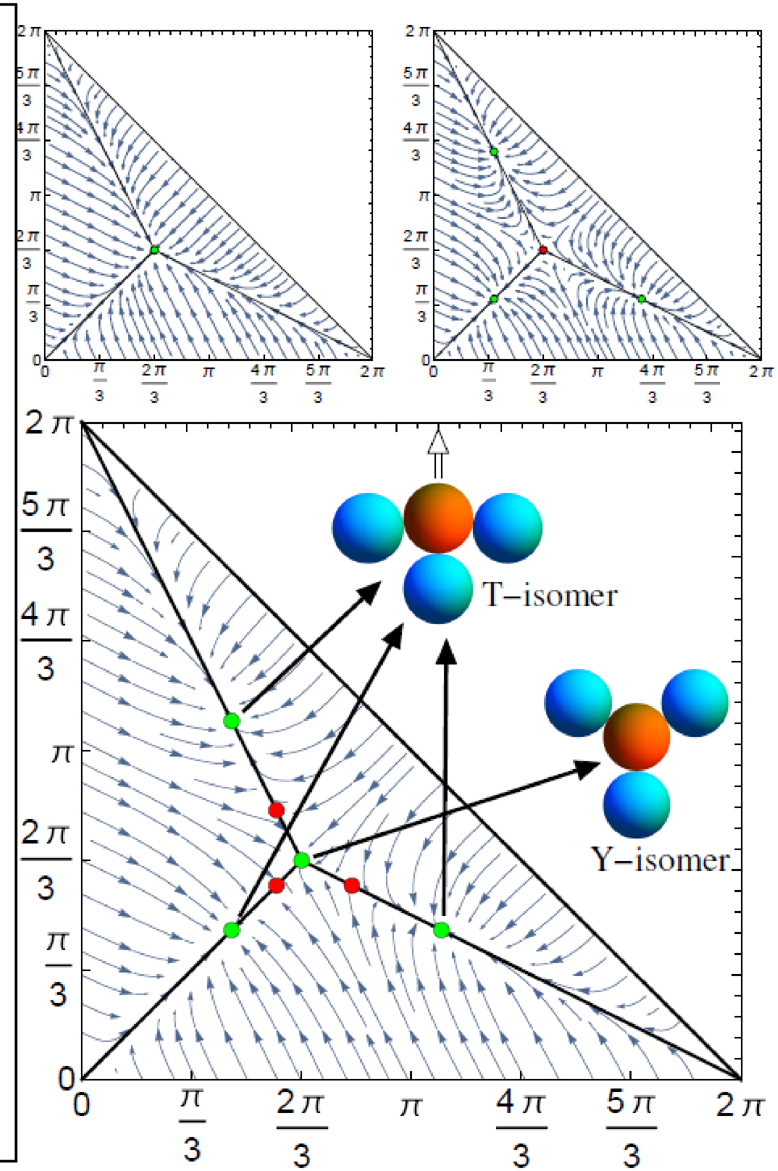
Inert molecules



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

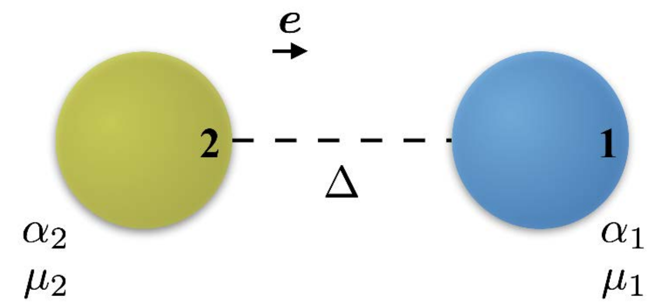
R. Soto & R. Golestanian (2014)

Dynamic Function: Run & Tumble



'Far-field' solution – Relative motion

$$\boldsymbol{V}_{\text{rel}} = \frac{R^2 \boldsymbol{e}}{D\left(\Delta + 2R\right)^2}\left(\alpha_2\mu_1 + \alpha_1\mu_2\right)$$

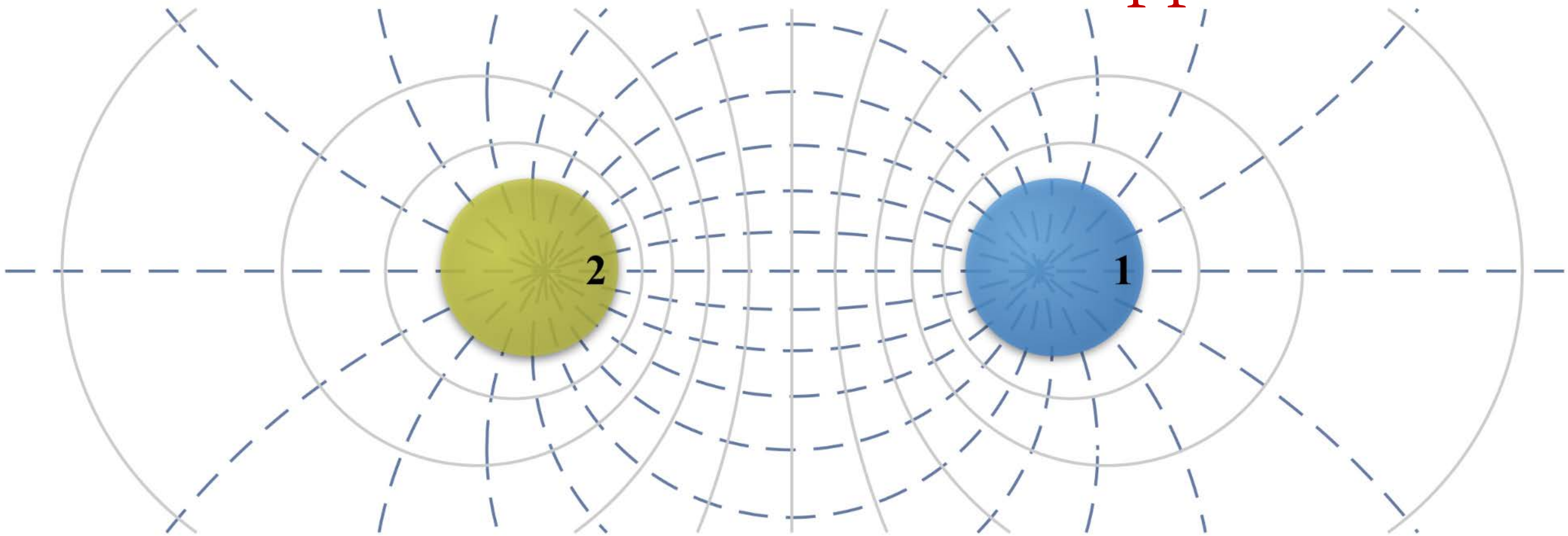


Regime I: Attraction $\alpha_2\mu_1 + \alpha_1\mu_2 < 0$

Regime II: Repulsion $\alpha_2\mu_1 + \alpha_1\mu_2 > 0$

► **What happens when the particles are close?**

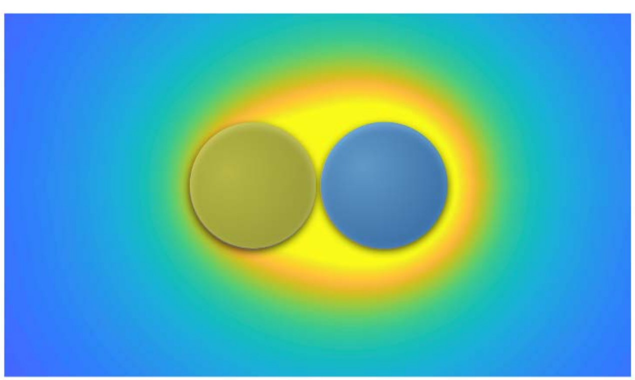
Chemical interaction – Exact approach

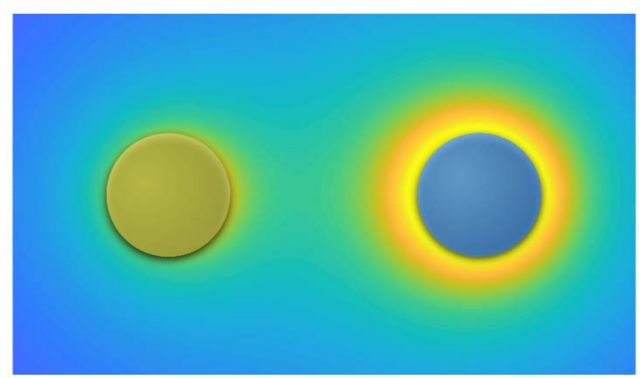


- Can be solved exactly using bi-spherical coordinate system

$$\nabla^2 C = 0$$

$$\text{B.C.} \begin{cases} -D\boldsymbol{n}_1 \cdot \boldsymbol{\nabla} C|_{\mathcal{S}_1} = \alpha_1 \\ -D\boldsymbol{n}_2 \cdot \boldsymbol{\nabla} C|_{\mathcal{S}_2} = \alpha_2 \end{cases}$$





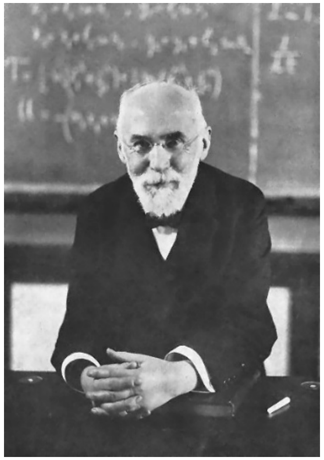
Hydrodynamic interaction – Exact approach

$$\eta\nabla^2 \boldsymbol{v} = \boldsymbol{\nabla} p, \quad \boldsymbol{\nabla}\cdot\boldsymbol{v} = 0 \longrightarrow \boxed{\nabla^4\psi = 0}$$

B.C.
$$\begin{cases} \boldsymbol{v}|_{\mathcal{S}_1} = \boldsymbol{V}_1 + \boxed{\boldsymbol{v}_1^{\mathrm{s}}} \\ \boldsymbol{v}|_{\mathcal{S}_2} = \boldsymbol{V}_2 + \boxed{\boldsymbol{v}_2^{\mathrm{s}}} \end{cases}$$

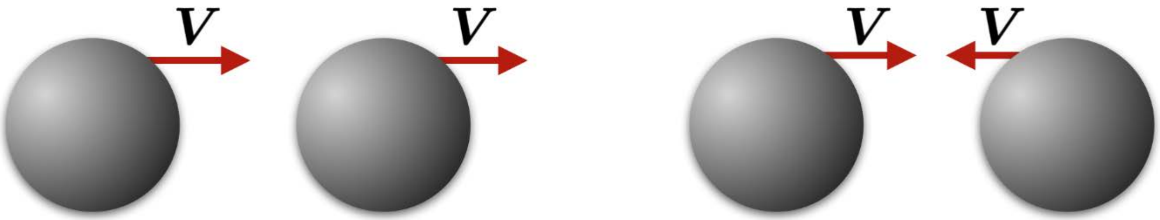
Expensive to solve!

Lorentz Reciprocal Theorem



H. A. Lorentz (1853-1928)

- Using the reciprocal theorem, we don't need to solve the Stokes equations directly
- We only need to know the full solution to two auxiliary problems:



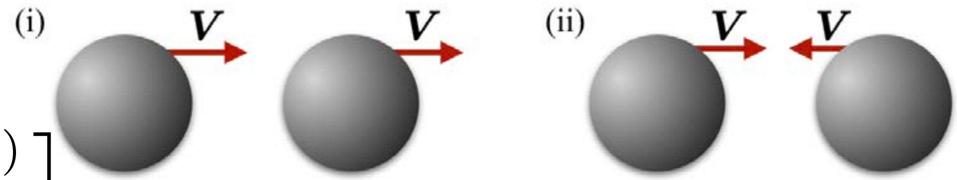
Exact Solution

Chemical interactions:

$$C(\boldsymbol{x}) = \alpha_1 \mathcal{G}_1(\boldsymbol{x} - \boldsymbol{x}_1) + \alpha_2 \mathcal{G}_2(\boldsymbol{x} - \boldsymbol{x}_2) \qquad \mathcal{G}_1 = \mathcal{G}_2^*$$

$$\boldsymbol{v}_k^{\mathrm{s}} = \mu_k \alpha_k \boldsymbol{\nabla}_{\|}^{k} \mathcal{G}_k(R\boldsymbol{n}_k) + \mu_k \alpha_l \boldsymbol{\nabla}_{\|}^{k} \mathcal{G}_l(R\boldsymbol{n}_k + \boldsymbol{x}_k - \boldsymbol{x}_l)$$

Hydrodynamic interactions:



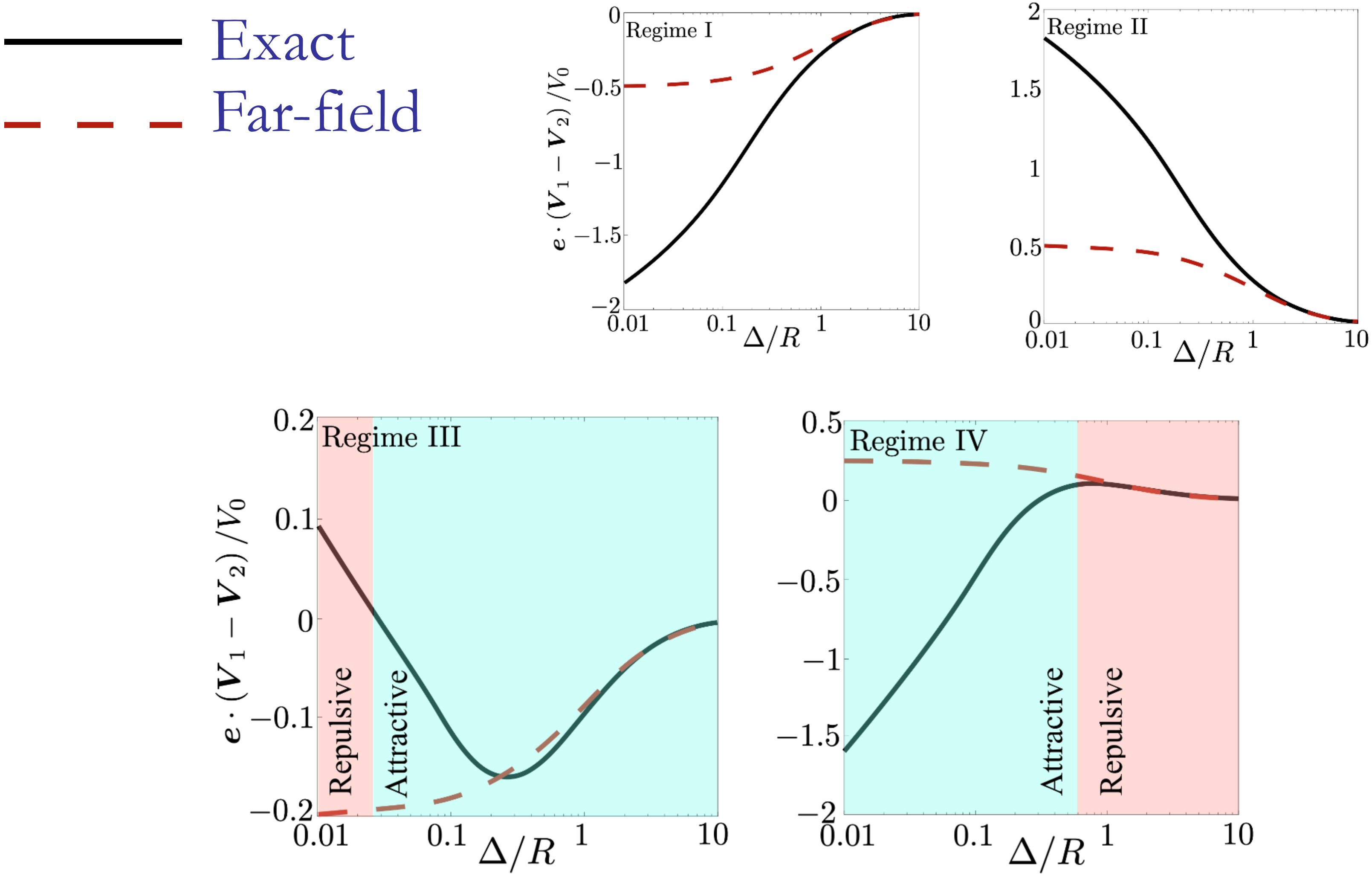
$$\begin{bmatrix} \boldsymbol{V}_1 \\ \boldsymbol{V}_2 \end{bmatrix} = - \begin{bmatrix} \boldsymbol{F}_1^{(\mathrm{i})} & \boldsymbol{F}_2^{(\mathrm{i})} \\ \boldsymbol{F}_1^{(\mathrm{ii})} & \boldsymbol{F}_2^{(\mathrm{ii})} \end{bmatrix}^{-1} \cdot \begin{bmatrix} \mathcal{T}^{(\mathrm{i})} \\ \mathcal{T}^{(\mathrm{ii})} \end{bmatrix}$$

$$\mathcal{T}^{(a)} = \sum_{k=1}^{2} \left\langle \boldsymbol{n}_k \cdot \boldsymbol{\sigma}^{(a)} \cdot \boldsymbol{v}_k^{\mathrm{s}} \right\rangle_{\mathcal{S}_k}$$

$\boldsymbol{F}_1^{(\mathrm{i})} = \boldsymbol{F}_2^{(\mathrm{i})} =$ Hydrodynamic forces on the particles in the trailing problem

$\boldsymbol{F}_1^{(\mathrm{ii})} = -\boldsymbol{F}_2^{(\mathrm{ii})} =$ Hydrodynamic forces on the particles in the approaching problem

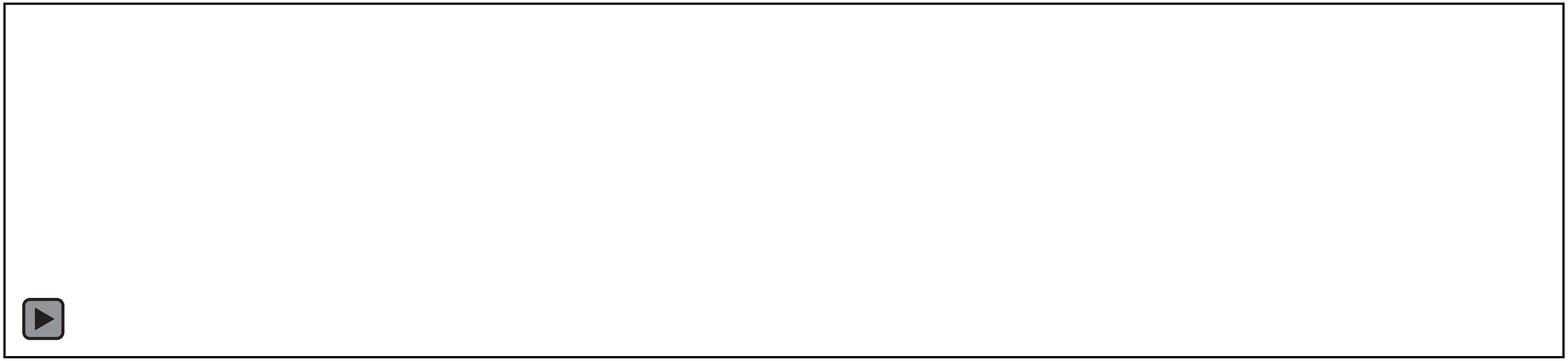
Exact solution – Relative motion



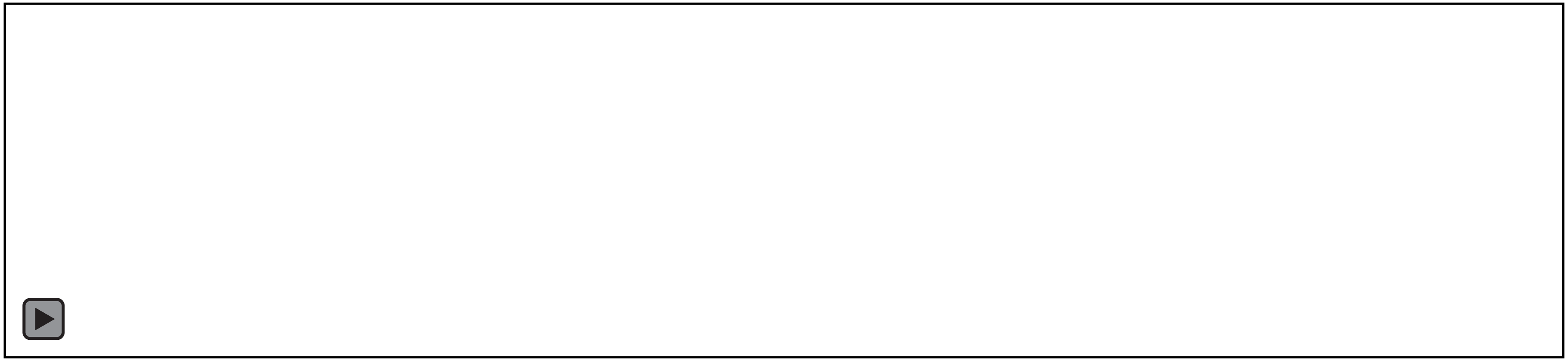
► **Emergence of two new regimes, with stable and unstable fixed-points**

Exact solution – Relative motion

Regime III: Stable fixed-point



Regime IV: Unstable fixed-point



What is different?

Far-field solution:

$$\boldsymbol{V}_{\mathrm{rel}} = \frac{R^2 \boldsymbol{e}}{D\left(\Delta + 2R\right)^2}\left(\alpha_2\mu_1 + \alpha_1\mu_2\right)$$

Exact solution:

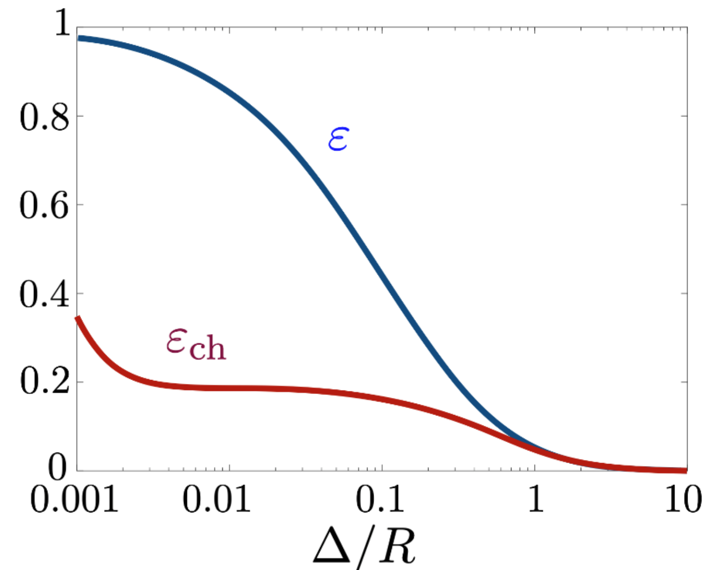
$$\boldsymbol{V}_{\mathrm{rel}} = \frac{\mathcal{F}\boldsymbol{e}}{\left|\boldsymbol{F}_1^{(\mathrm{ii})}\right|}\left[\left(\alpha_2\mu_1 + \alpha_1\mu_2\right) + \varepsilon\left[\Delta\right]\left(\alpha_1\mu_1 + \alpha_2\mu_2\right)\right]$$

Exact chemical/no hydrodynamic:

$$\boldsymbol{V}_{\mathrm{rel}} = \frac{\mathcal{F}_{\mathrm{ch}}\boldsymbol{e}}{4\pi R^2}\left[\left(\alpha_2\mu_1 + \alpha_1\mu_2\right) + \varepsilon_{\mathrm{ch}}\left[\Delta\right]\left(\alpha_1\mu_1 + \alpha_2\mu_2\right)\right]$$

$$\varepsilon = \frac{\mathcal{N}}{\mathcal{F}} = \frac{\left\langle \sigma_k^{(\mathrm{ii})}\boldsymbol{\nabla}_{\parallel}^{k}\mathcal{G}_k\left(R\boldsymbol{n}_k\right)\cdot\boldsymbol{t}_k\right\rangle_{\mathcal{S}_k}}{\left\langle \sigma_k^{(\mathrm{ii})}\boldsymbol{\nabla}_{\parallel}^{k}\mathcal{G}_l\left(R\boldsymbol{n}_k + \boldsymbol{x}_k - \boldsymbol{x}_l\right)\cdot\boldsymbol{t}_k\right\rangle_{\mathcal{S}_k}}$$

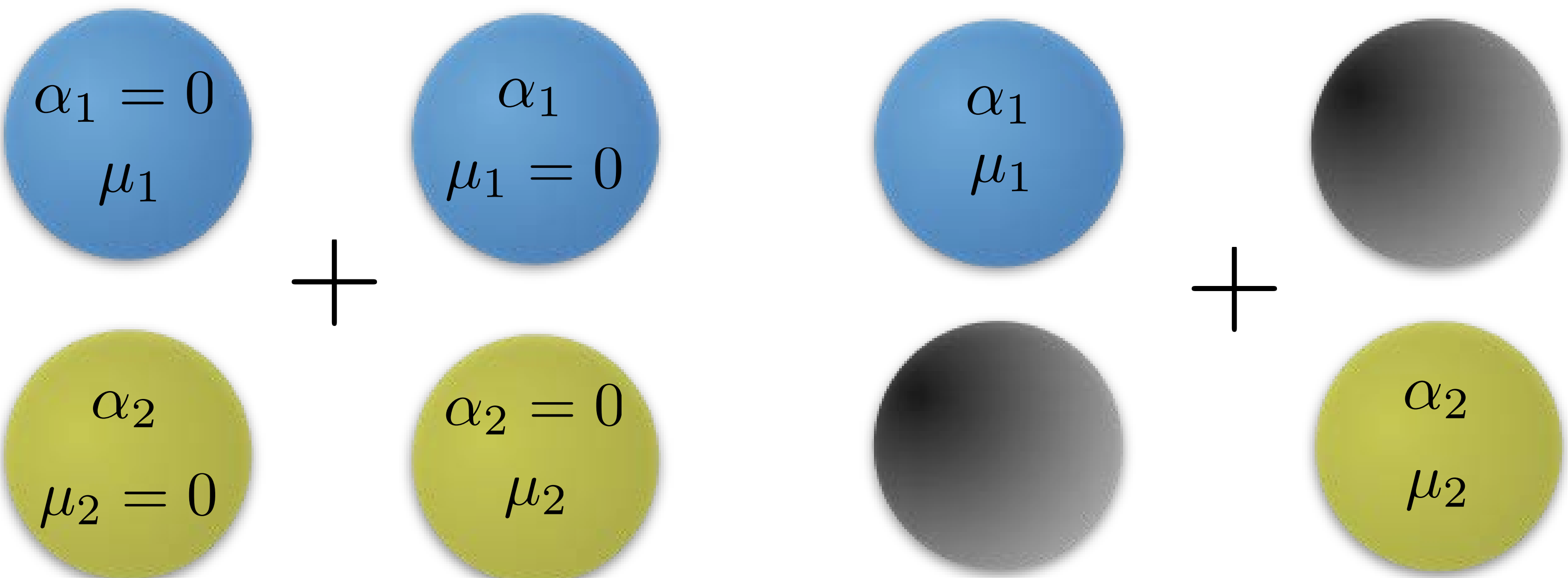
$$\varepsilon_{\mathrm{ch}} = \frac{\mathcal{N}_{\mathrm{ch}}}{\mathcal{F}_{\mathrm{ch}}} = \frac{(-1)^k\left\langle \boldsymbol{\nabla}_{\parallel}^{k}\mathcal{G}_k\left(R\boldsymbol{n}_k\right)\cdot\boldsymbol{t}_k\right\rangle_{\mathcal{S}_k}}{(-1)^{k+1}\left\langle \boldsymbol{\nabla}_{\parallel}^{k}\mathcal{G}_l\left(R\boldsymbol{n}_k + \boldsymbol{x}_k - \boldsymbol{x}_l\right)\cdot\boldsymbol{t}_k\right\rangle_{\mathcal{S}_k}}$$



Why is it happening?

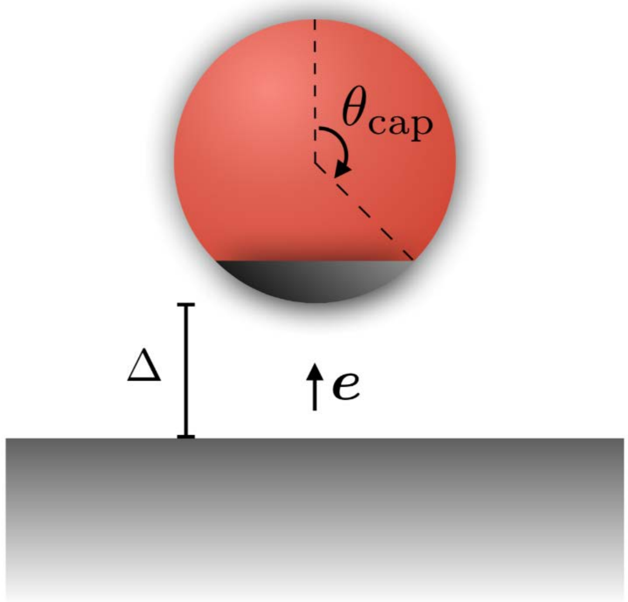
$$\boldsymbol{V}_{\text{rel}} = \frac{\mathcal{F}\boldsymbol{e}}{\left|\boldsymbol{F}_1^{(\text{ii})}\right|}\left[(\alpha_2\mu_1 + \alpha_1\mu_2) + \varepsilon\,[\Delta]\,(\alpha_1\mu_1 + \alpha_2\mu_2)\right]$$

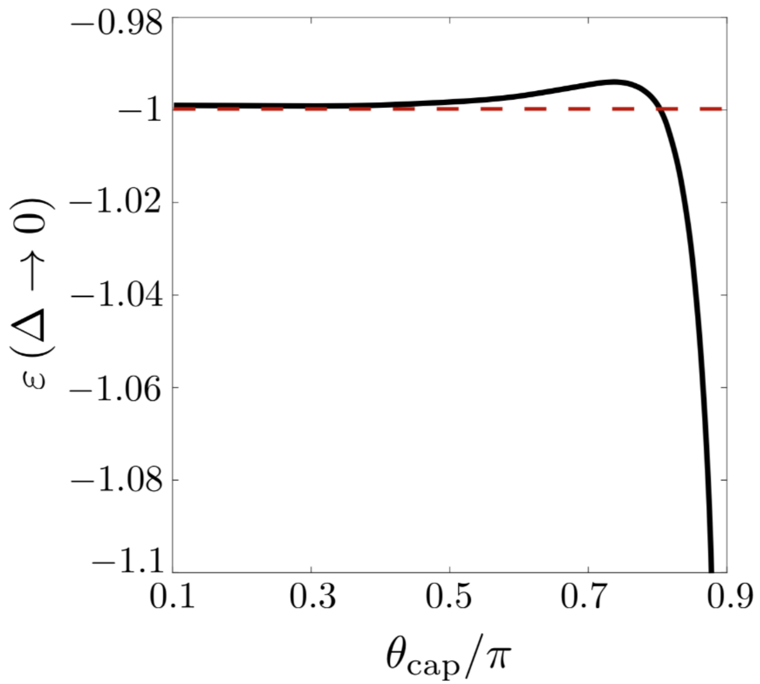
Far-field effect **Near-field effect**



- **Near-field effect is captured by a self-generated neighbour-reflected term**

Similar to a Janus particle near wall





Concentration field with no wall

Wall correction

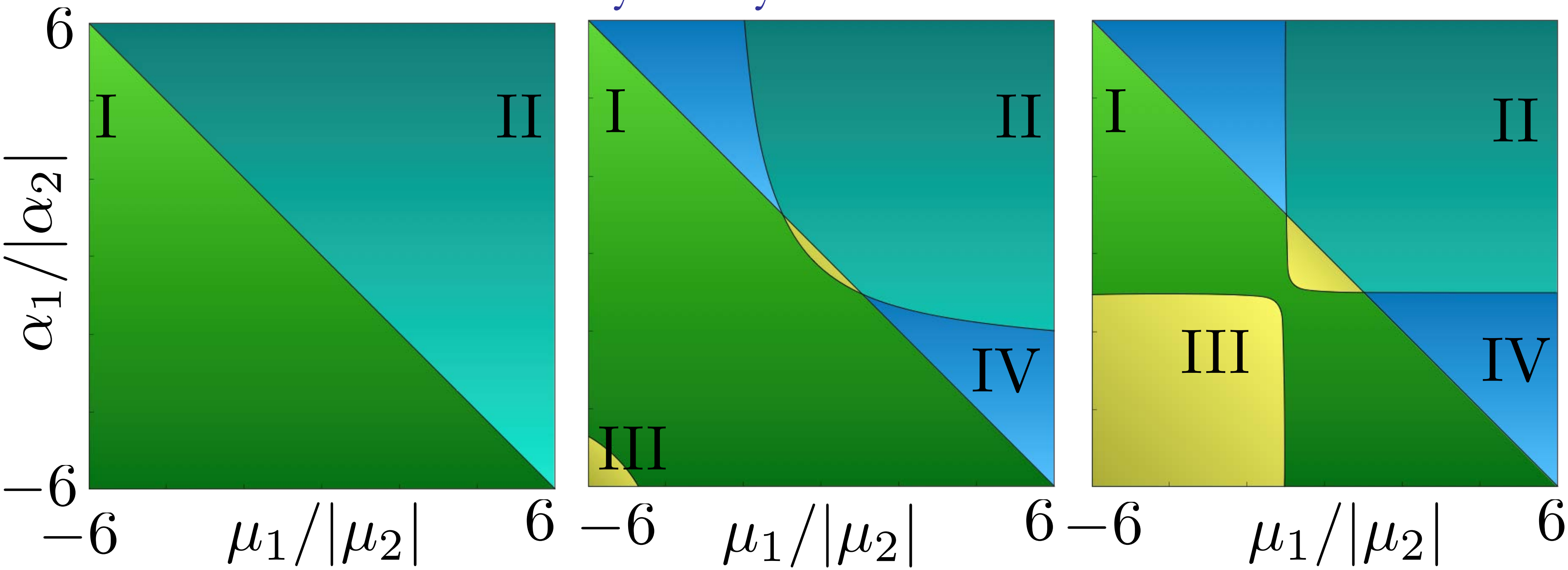
$$C(\boldsymbol{x}) = C_1(\boldsymbol{x}) + C_2(\boldsymbol{x})$$

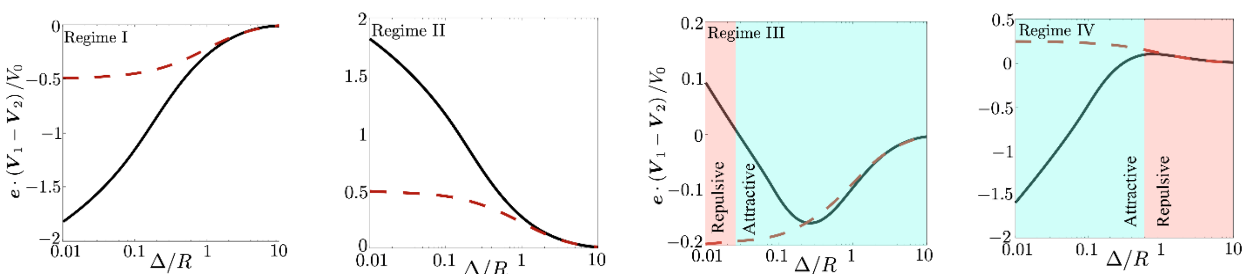
$$\boldsymbol{V} = \frac{-\mu \mathcal{F} \boldsymbol{e}}{\hat{\boldsymbol{F}} \cdot \boldsymbol{e}}(1+\varepsilon)$$

$$\varepsilon \equiv \frac{\text{wall effects}}{\text{self-propulsion}} = \frac{\mathcal{N}}{\mathcal{F}} = \frac{\langle \boldsymbol{n} \cdot \hat{\boldsymbol{\sigma}} \cdot \boldsymbol{\nabla}_{\parallel} C_2 \rangle}{\langle \boldsymbol{n} \cdot \hat{\boldsymbol{\sigma}} \cdot \boldsymbol{\nabla}_{\parallel} C_1 \rangle}$$

Where in parameter space?

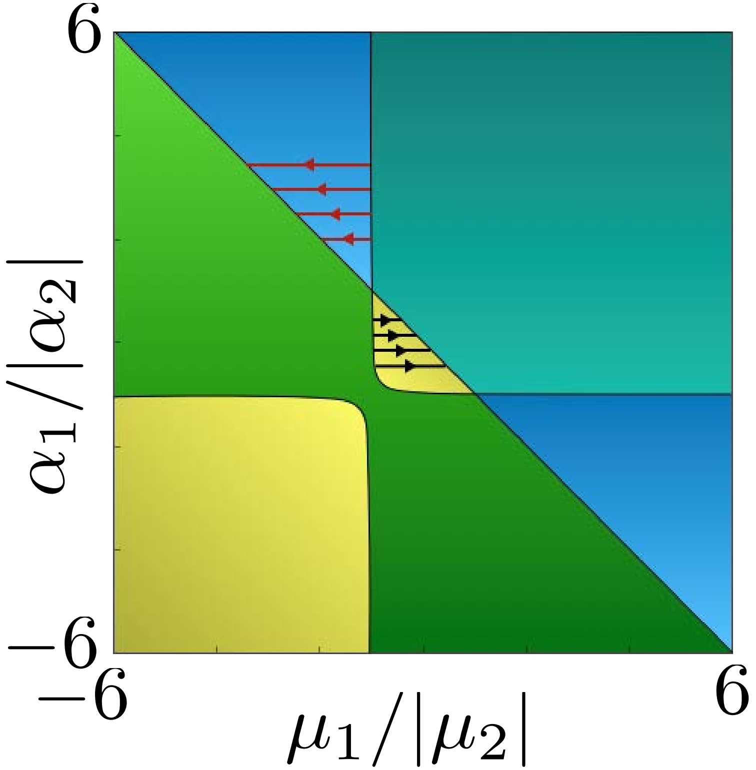
- Far-field
- Exact chemical/no hydrodynamic
- Full solution

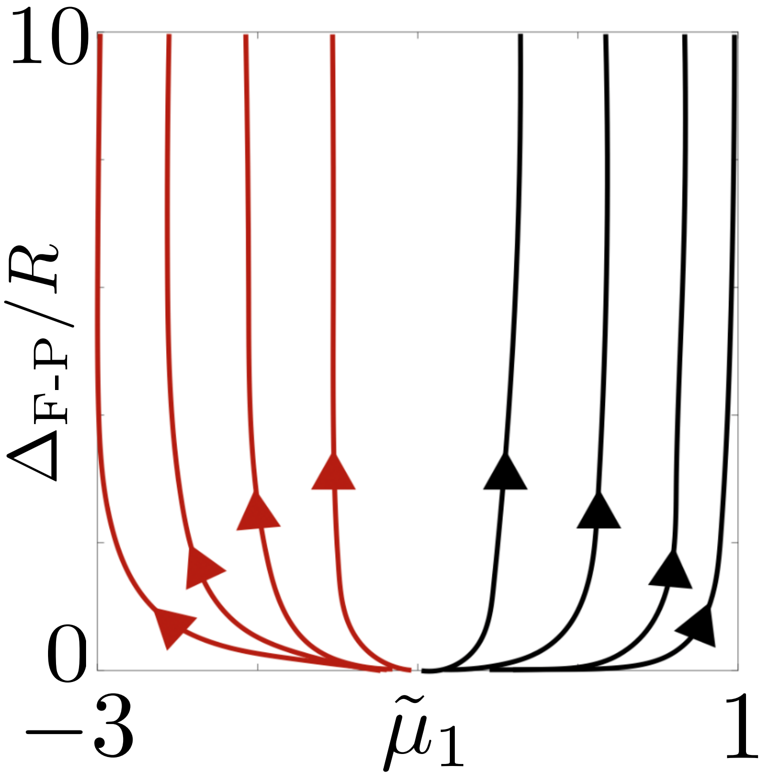




Fixed-point variation

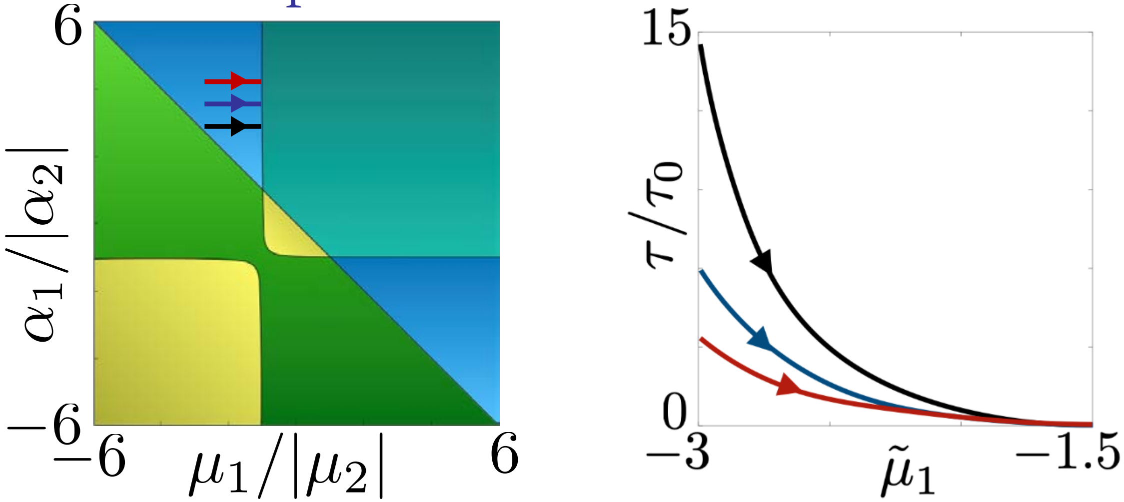
- In regime III and IV, the fixed-point tends to zero or infinity upon reaching the regime boundaries



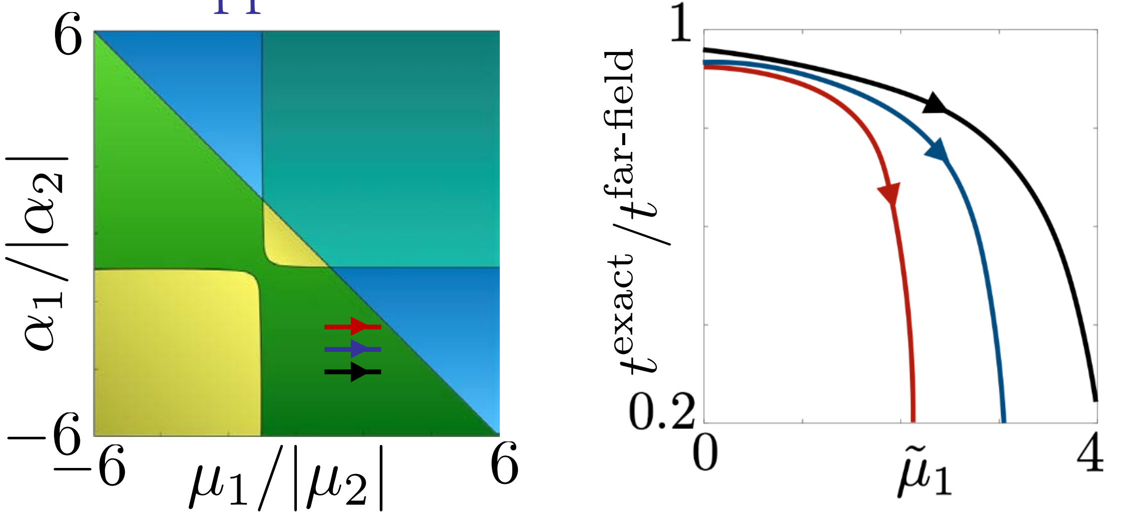


Escape & collapse time

- *First-passage time*: time needed to break apart a complex formed in regime IV in the presence of noise



- *Collapse time*: comparing the collapse time in regime I, using the exact and far-field approach



► Remarks

- Near-field effects can qualitatively change the behaviour of the system
- Due to near-field effects, a fixed-point may emerge in the dynamical system which can be stable (Regime III) or unstable (Regime IV)
- In the absence of hydrodynamic interactions, near-field chemical interactions can still capture the new regimes
- Near-field effects are due to a self-generated neighbour-reflected term
- Outlook: near-field effects in many-body interactions…