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

Chemically-active particles

If $\lambda/R \ll 1$, surface activity can be captured by local slip velocity ($v^s$).

$$V = -\frac{1}{A} \langle v^s \rangle$$
Activity and Mobility

Chemical Activity ($\alpha$):
- Characterizes how it produces or consumes chemicals

Chemical Mobility ($\mu$):
- 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

\[ V = 0 \]
Pair interactions

Chemical interactions:
- Diffusion Equation

Hydrodynamic interactions:
- Stokes Equations

Slip Velocities
Pair interactions

Chemical interactions:

\[ \nabla^2 C = 0 \]

B.C.

\[ \begin{align*}
-D n_1 \cdot \nabla C|_{S_1} &= \alpha_1 \\
-D n_2 \cdot \nabla C|_{S_2} &= \alpha_2
\end{align*} \]

Hydrodynamic interactions:

\[ \begin{align*}
\eta \nabla^2 \mathbf{v} &= \nabla \rho \\
\nabla \cdot \mathbf{v} &= 0
\end{align*} \]

B.C.

\[ \begin{align*}
\mathbf{v}|_{S_1} &= \mathbf{V}_1 + \mathbf{v}_1^s \\
\mathbf{v}|_{S_2} &= \mathbf{V}_2 + \mathbf{v}_2^s
\end{align*} \]

\[ \begin{align*}
\mathbf{v}_1^s &= \mu_1 (I - n_1 n_1) \cdot \nabla C \\
\mathbf{v}_2^s &= \mu_2 (I - n_2 n_2) \cdot \nabla C
\end{align*} \]
Assumptions:

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

\[
V_1 = \frac{R^2 e}{D (\Delta + 2R)^2} \alpha_2 \mu_1 \\
V_2 = \frac{-R^2 e}{D (\Delta + 2R)^2} \alpha_1 \mu_2
\]
$AB, AB_2, AB_3, \ldots, AB_n$

$A \quad \tilde{\alpha}_A = 3$

$\tilde{\mu}_A = 0$

$B \quad \tilde{\alpha}_B = \tilde{\mu}_B = -1$
Tabulating Active Molecules

Translational propulsion

Rotational propulsion

Inert molecules

3D Structure determines Function, like proteins

Dynamic Function: Run & Tumble

‘Far-field’ solution – Relative motion

\[ V_{\text{rel}} = \frac{R^2 e}{D (\Delta + 2R)^2} (\alpha_2 \mu_1 + \alpha_1 \mu_2) \]

**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

\[ \nabla^2 C = 0 \]

B.C. \quad \begin{cases} 
-Dn_1 \cdot \nabla C|_{S_1} = \alpha_1 \\
-Dn_2 \cdot \nabla C|_{S_2} = \alpha_2 
\end{cases}
Hydrodynamic interaction – Exact approach

\[ \eta \nabla^2 \mathbf{v} = \nabla p \]
\[ \nabla \cdot \mathbf{v} = 0 \]

\[ \nabla^4 \psi = 0 \]

\[ \mathbf{v}|_{S_1} = \mathbf{V}_1 + \mathbf{v}^s_1 \]
\[ \mathbf{v}|_{S_2} = \mathbf{V}_2 + \mathbf{v}^s_2 \]

Expensive to solve!

Lorentz Reciprocal Theorem

- 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:

\[ C(x) = \alpha_1 g_1(x - x_1) + \alpha_2 g_2(x - x_2) \quad \quad \quad g_1 = g_2^* \]

\[ \mathbf{v}_k^s = \mu_k \alpha_k \nabla^k g_k(Rn_k) + \mu_k \alpha_l \nabla^k g_l(Rn_k + x_k - x_l) \]

Hydrodynamic interactions:

\[
\begin{bmatrix}
V_1 \\
V_2
\end{bmatrix} = - \begin{bmatrix}
F_{1}^{(i)} & F_{2}^{(i)} \\
F_{1}^{(ii)} & F_{2}^{(ii)}
\end{bmatrix}^{-1} \cdot \begin{bmatrix}
\mathcal{T}^{(i)} \\
\mathcal{T}^{(ii)}
\end{bmatrix}
\]

\[ \mathcal{T}^{(a)} = \sum_{k=1}^{2} \left\langle n_k \cdot \sigma^{(a)} \cdot \mathbf{v}_k^s \right\rangle_{S_k} \]

\[ F_1^{(i)} = F_2^{(i)} = \text{Hydrodynamic forces on the particles in the trailing problem} \]

\[ F_1^{(ii)} = -F_2^{(ii)} = \text{Hydrodynamic forces on the particles in the approaching problem} \]
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:

\[ V_{\text{rel}} = \frac{R^2 e}{D (\Delta + 2R)^2} (\alpha_2 \mu_1 + \alpha_1 \mu_2) \]

Exact solution:

\[ V_{\text{rel}} = \frac{\mathcal{F} e}{|\mathcal{F}_{1}^{(ii)}|} \left[ (\alpha_2 \mu_1 + \alpha_1 \mu_2) + \varepsilon [\Delta] (\alpha_1 \mu_1 + \alpha_2 \mu_2) \right] \]

Exact chemical/no hydrodynamic:

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

\[ \varepsilon = \frac{\mathcal{N}}{\mathcal{F}} = \frac{\left\langle \sigma_k^{(ii)} \nabla^k \mathcal{G}_k (Rn_k) \cdot t_k \right\rangle_{S_k}}{\left\langle \sigma_k^{(ii)} \nabla^k \mathcal{G}_l (Rn_k + x_k - x_l) \cdot t_k \right\rangle_{S_k}} \]

\[ \varepsilon_{\text{ch}} = \frac{\mathcal{N}_{\text{ch}}}{\mathcal{F}_{\text{ch}}} = \frac{(-1)^k \left\langle \nabla^k \mathcal{G}_k (Rn_k) \cdot t_k \right\rangle_{S_k}}{(-1)^{k+1} \left\langle \nabla^k \mathcal{G}_l (Rn_k + x_k - x_l) \cdot t_k \right\rangle_{S_k}} \]
Why is it happening?

\[ V_{\text{rel}} = \frac{\mathcal{F}e}{|F_1^{(ii)}|} \left[ (\alpha_2 \mu_1 + \alpha_1 \mu_2) + \varepsilon [\Delta] (\alpha_1 \mu_1 + \alpha_2 \mu_2) \right] \]

Far-field effect

\[ \alpha_1 = 0 \]
\[ \mu_1 \]

\[ \alpha_1 \]
\[ \mu_1 = 0 \]

\[ \alpha_2 \]
\[ \mu_2 = 0 \]

Near-field effect

\[ \alpha_1 \]
\[ \mu_1 \]

\[ \alpha_2 \]
\[ \mu_2 \]

Near-field effect is captured by a self-generated neighbour-reflected term
Similar to a Janus particle near wall

Concentration field with no wall

\[ C(\mathbf{x}) = C_1(\mathbf{x}) + C_2(\mathbf{x}) \]

Wall correction

\[ \mathbf{V} = \frac{-\mu \mathcal{F} \mathbf{e}}{\hat{\mathbf{F}} \cdot \mathbf{e}} (1 + \varepsilon) \]

\[ \varepsilon \equiv \frac{\text{wall effects}}{\text{self-propulsion}} = \frac{\mathcal{N}}{\mathcal{F}} = \frac{\langle \mathbf{n} \cdot \hat{\mathbf{\sigma}} \cdot \nabla \parallel C_2 \rangle}{\langle \mathbf{n} \cdot \hat{\mathbf{\sigma}} \cdot \nabla \parallel C_1 \rangle} \]
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…