Effective Interactions Between Chemically Active Colloids and Surfaces

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Chemically active colloids: synthetic micro-motors

- Scaling down standard machinery: need to enable small-scale objects to perform *autonomous, controlled* motion --> micro- or nano-carriers

- **Biological nano-motors**:  
  *kinesin* motor protein
  
  - extract chemical free energy from surrounding medium (catalytic reaction)
  - convert it to mechanical work (power directed motion) by coupling to a source of asymmetry

- **Chemically active colloids**: *synthetic* “motors”, functioning on *similar principle*
Example of a chemically active Janus colloid:

silica – Pt spheres decomposing $\text{H}_2\text{O}_2$ in water

Plausible mechanism: self-phoresis

simplest case: self-diffusiophoresis (density gradients of neutral solute species)
Self-diffusiophoresis of chemically active colloids: Minimal Model

- impermeable particle, catalytic region
- immersed in a Newtonian solution of viscosity $\mu$
- catalyst promotes a chemical “creation” of a product (solute) $A$ in the surrounding solution
- solute molecules are diffusing in the solution
- solute molecule ($A$) – particle interaction $\varphi_A$
  $\neq$ solvent molecules ($S$) – particle ones $\varphi_S$
- contact with reservoir(s) of solvent/solute
- no external forces or torques on particle or solution

- constant temperature $T$
- time & space independent mass density $\rho$ of solution

- Distribution of solute by diffusion $c(r)$
- Hydrodynamic flow of solution $u(r)$
- Motion of particle $U, \Omega$
Separation of time scales

Typical size of particles: \( R \sim 1 - 5 \, \mu m \)

particle velocities: \( U \lesssim 10 \, \mu m/s \) (experimental observations)

solute diffusion constant: \( D \sim 10^{-9} \, m^2/s \) (small molecules in water-like-viscosity solvent)

Time scales:

diffusion of solute: \( t_{diff} = \frac{R^2}{D} \sim 10^{-3} \, s \)

translational diffusion of particle: \( \tau_d \sim 10 \, s \)

rotational diffusion of the symmetry axis (particle): \( \tau_r \sim 10 - 100 \, s \)

drift of particle: \( t_{drift} = \frac{R}{U} \gtrsim 10^{-1} \, s \)

- quasi-steady state distribution of solute
- translational diffusion can be neglected
- rotational diffusion important at long times
Reynolds (inertial/viscous) and Péclet (advection/diffusion) numbers

Typical solvent: $\mu \sim 10^{-3}$ Pa s, $\rho \sim 10^3$ kg/m$^3$

$$Re = \frac{\rho RU}{\mu} \sim 10^{-5}$$

- *creeping flow (Stokes) equations* for hydrodynamics

$$Pe = \frac{RU}{D} \sim 10^{-2}$$

- advective solute current negligible

$=>$ *solute diffusion decouples from hydrodynamics*
Self-diffusiophoresis of chemically active colloid


- Result of surface forces (interfacial phenomena) + non-equilibrium solute gradients

\[ \Phi(r) \] steeply decaying with the distance from the surface

\[ \beta \Phi(r) \ll 1 \] within a distance \( \delta \ll R \) from \( S_P \)

**Phoretic slip** (hydrodynamic boundary condition at the surface of particle)

\[ u_s(r_P) = -\frac{\mathcal{L}(r_P)}{\beta \mu} \nabla_{||} c(r_P) := -b(r_P) \nabla_{||} c(r_P) \]

\( < 0 \) (\( > 0 \)) : repulsive (attractive) interaction
Active colloids near surfaces

- Typical experimental realisations: the active colloids are residing near the boundaries of the vessel (e.g., confined in micro-channels, sedimented, ...)

- Chemical activity and “inert” boundary:
  - solute distribution and hydrodynamic flows modified by boundaries

\[(activity \iff boundary) \text{ leads to}\]

- surface-bounded steady-states of motion: sliding, hovering
- rheotactic behavior for spherical active particles

**Self-diffusiophoresis near a hard wall**

**Assumption:** quasi-adiabatic motion, $\mathbf{U}$ and $\mathbf{\Omega}$ sufficiently small that diffusion and hydrodynamics can be treated as steady states corresponding to sphere at $(h, \theta)$

**Distribution of solute**

\[ \nabla^2 c = 0 \]
\[ \mathbf{n} \cdot [-D \nabla c(\mathbf{r})]_{\text{active}} = k \]
\[ \mathbf{n} \cdot [-D \nabla c(\mathbf{r})]_{\text{inert}} = 0 \]
\[ \mathbf{n} \cdot [-D \nabla c(\mathbf{r})]_{\text{wall}} = 0 \]
\[ c(|\mathbf{r}| \to \infty) = 0 \]

**Hydrodynamics**

\[ \nabla \cdot \mathbf{\sigma} = 0, \quad \nabla \mathbf{u} = 0 \]
\[ \mathbf{\sigma} := \mu \left[ \nabla \mathbf{u} + (\nabla \mathbf{u})^\dagger \right] - p \mathbf{I} \]
\[ \mathbf{u}_{\text{particle}} = \mathbf{V} + \mathbf{\Omega} \times (\mathbf{r} - \mathbf{r}_O) + \mathbf{u}_s \]
\[ \mathbf{u}_{\text{wall}} = 0 \]
\[ \mathbf{u}(|\mathbf{r}| \to \infty) = 0 \]

- **Self-”propulsion”: no net external force or torque acting on the particle**
- **Numerical (Boundary Element Method) solutions for both diffusion and hydrodynamics**
Lorenz reciprocal theorem. Calculation of self-diffusiophoretic velocities

(Brenner, Low Reynolds number hydrodynamics)

- **Stokes force-free equations within a given domain** \( D \)

- **Two incompressible flows, for different boundary conditions on** \( \partial D \)

\[
\int_{\partial D} \mathbf{u} \cdot \mathbf{\sigma}_a \cdot \mathbf{n} \, dS = \int_{\partial D} \mathbf{u}_a \cdot \mathbf{\sigma} \cdot \mathbf{n} \, dS
\]

(version including volume forces: Kim & Karilla, *Microhydrodynamics*)
Lorenz reciprocal theorem. Calculation of self-diffusiophoretic velocities

\[
\int_{\partial \mathcal{D}} \mathbf{u} \cdot \mathbf{\nabla}_a \cdot \mathbf{n} \, dS = \int_{\partial \mathcal{D}} \mathbf{u}_a \cdot \mathbf{\nabla} \cdot \mathbf{n} \, dS
\]

- The active particle: first problem; an identical shape, but inactive particle: the auxiliary problem

- Auxiliary problem: constant \( \mathbf{V}_a, \mathbf{\Omega}_a \) [force and torque exerted on particle by the fluid \( \mathbf{F}_a, \mathbf{T}_a \)]

- \( \mathbf{u}, \mathbf{u}_a \): decay at least as fast as \( 1/r \) => no contributions from the integrals over surface at \( \infty \)

- On wall: \( \mathbf{u}, \mathbf{u}_a \) vanish => no contribution from integrals over the wall

- On particle: \( \mathbf{u} = \mathbf{u}_s + \mathbf{V} + \mathbf{\Omega} \times (\mathbf{r}_P - \mathbf{r}_O) \) \( \mathbf{u}_a = 0 + \mathbf{V}_a + \mathbf{\Omega}_a \times (\mathbf{r}_P - \mathbf{r}_O) \) \( \nabla \cdot \mathbf{F}_a + \mathbf{\Omega} \cdot \mathbf{T}_a = - \int_{S_P} \mathbf{u}_s \cdot \mathbf{n} \cdot dS \)

- 6 unknowns => 6 auxiliary problems:
  
  uniform translation (\( a = 1,2,3 \)) or rotation (\( a = 4,5,6 \)) along \( x, y, \) or \( z \)
Surface bounded steady-states: sliding

Inert wall, repulsive colloid-solute interactions:

- "sliding" state, "attractor" for a broad range of starting points (height and orientation)

\[ b(r) \]: constant < 0 over the surface
Surface bound steady-states: sliding

Experiment:

half-covered Pt/silica colloid, sliding state with $\theta \approx \pi/2$

Model:

phoretic mobility $b(r) < 0$ over the surface, $\beta = 0.3$

(provides additional mechanism for rotation of symmetry axis)
**Sliding state: identify contributions**

\[ \mathbf{V} \cdot \mathbf{F}_a + \Omega \cdot \mathbf{T}_a = - \int_{S_P} \mathbf{u}_s \cdot \mathbf{\tau}_a^t \cdot \mathbf{n} \, dS \quad a = 1,2,...,6 \]

- solve for \( \mathbf{V} \) and \( \Omega \) by inverting the “resistance matrix” (forces and torques)

\[ \text{row } \mathbf{R}_k := (\mathbf{F}'_{kx}, \mathbf{F}'_{ky}, \mathbf{F}'_{kz}, \tau'_{kx}, \tau'_{ky}, \tau'_{kz}) \quad k = 1,2,...,6 \]

- isolate free space (bulk liquid) and wall-reflected parts:

\[ c(\mathbf{r}) = c^f_s(\mathbf{r}) + \delta c(\mathbf{r}) \]

\[ \sigma'_a(\mathbf{r}) = \sigma'^f_s(\mathbf{r}) + \delta \sigma'_a(\mathbf{r}) \]

- focus on \( \Omega_x (\sim d\theta/dt) \); at the sliding state: \( \Omega_x = 0 \)

\[ \Omega_x = (\mathbf{R}^{-1})_{4,j} \int_{\text{particle}} b(\mathbf{r}) \nabla || c^f_s(\mathbf{r}) \cdot \sigma'^f_s \cdot \mathbf{n} \, dS \quad \leftarrow \text{free space} \]

\[ + (\mathbf{R}^{-1})_{4,j} \int_{\text{particle}} b(\mathbf{r}) \nabla || \delta c(\mathbf{r}) \cdot \sigma'^f_s \cdot \mathbf{n} \, dS \quad \leftarrow \text{hydrodynamic interaction} \]

\[ + (\mathbf{R}^{-1})_{4,j} \int_{\text{particle}} b(\mathbf{r}) \nabla || \delta c(\mathbf{r}) \cdot \sigma'_j \cdot \mathbf{n} \, dS \quad \leftarrow \text{“chemical” interaction} \]

\[ + (\mathbf{R}^{-1})_{4,j} \int_{\text{particle}} b(\mathbf{r}) \nabla || \delta c(\mathbf{r}) \cdot \delta \sigma'_j \cdot \mathbf{n} \, dS \quad \leftarrow \text{higher order coupling} \]
Sliding state: contributions

\[ \Omega_x = 0 \]

- Hydrodynamic interaction
- "Chemical" interaction
- Higher order coupling

None of them alone can lead to the sliding state \( \Omega_x = 0 \)
Conclusions

Emergence of sliding steady states, experimentally relevant, for chemically active particles

Result of a very intricate coupling between chemical activity, confinement by wall, and surface properties of the colloid:

\[ \text{wall} \rightarrow \text{state } (h, \theta) \rightarrow \text{dependent changes in solute distribution} \rightarrow \text{changes in phoretic slip on the particle} \rightarrow \text{changes in flow and hydrodynamic torque on the particle} \]