Thermal Fluctuations in Colloidal Suspensions and Reactive Liquid Mixtures

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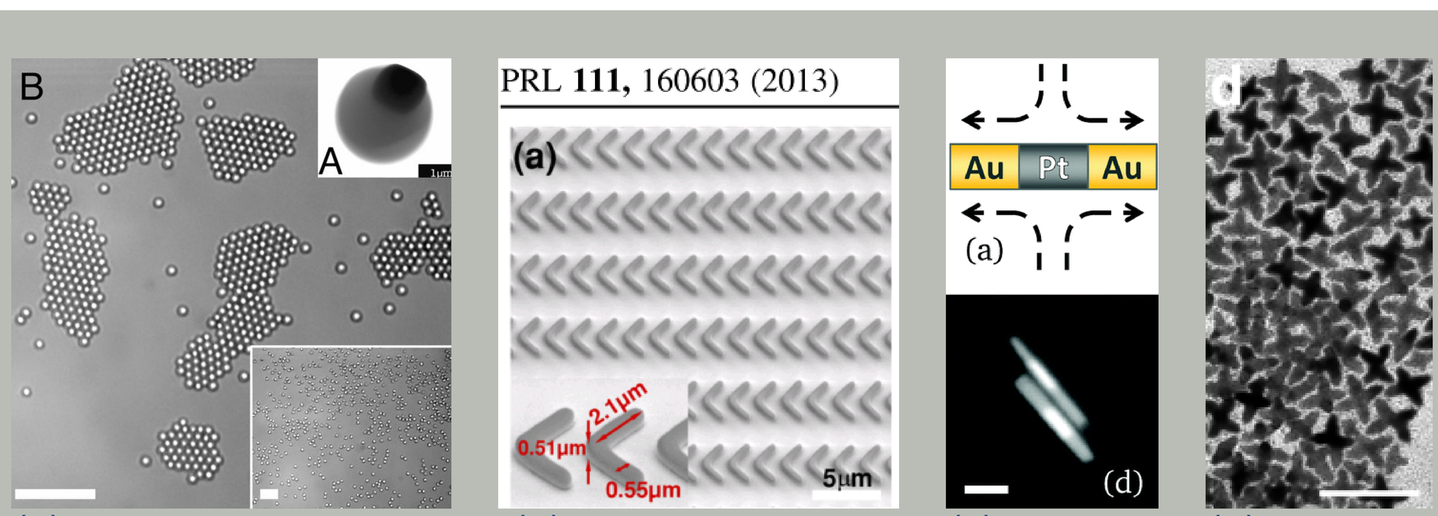
PART I. Colloidal Suspension



(a) Light-activated colloidal surfers (b) Colloidal boomerang (c) Active metallic rods (d) PbSe nanocrystals

Figure: (a) Palacci et al., 2013; (b) Chakrabarty et al., 2013; (c) Davies Wykes et al., 2016; (d) Shi et al., 2006.

The motion of N rigid particles immersed in a Stokesian fluid can be modeled by the **overdamped Langevin equation** of **Brownian Dynamics**,

$$\frac{d\mathbf{Q}}{dt} = \underbrace{\mathcal{N}\mathbf{F} + (2k_B T \mathcal{N})^{\frac{1}{2}} \mathcal{W}(t)}_{\text{Hydrodynamic interactions + Brownian increments}} + \underbrace{(k_B T)\, \partial_{\mathbf{Q}} \cdot \mathcal{N}}_{\text{Stochastic drift}},$$

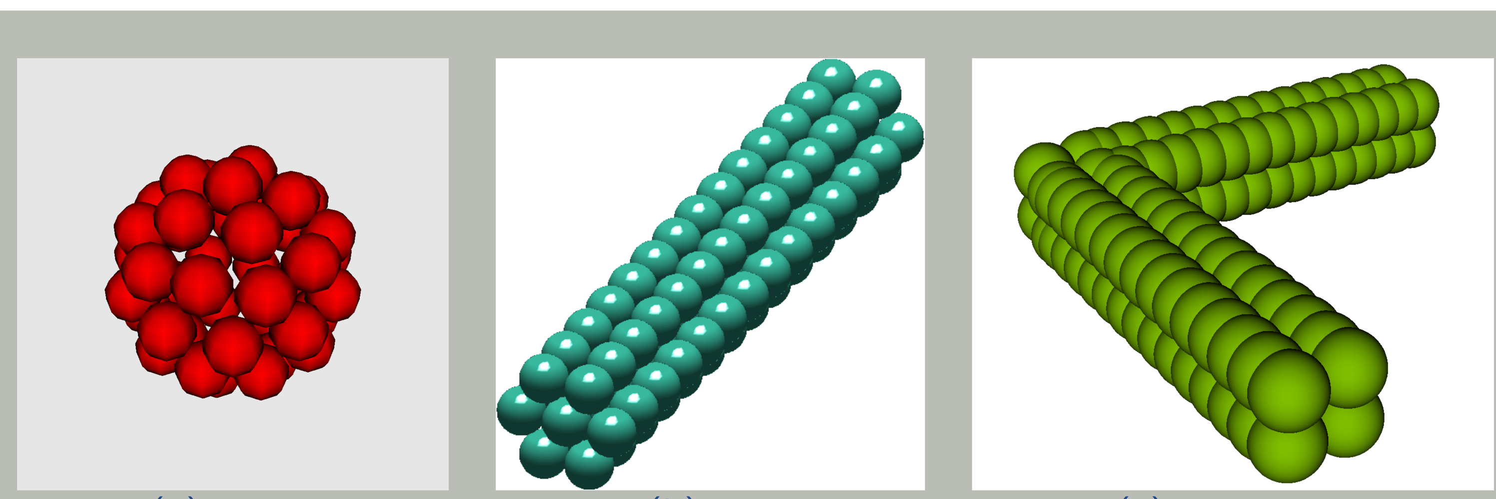
- $\mathbf{Q} = \{\mathbf{q}_\beta, \theta_\beta\}_{\beta=1}^N$ consists of **positions** and **orientations** of particles, $\mathbf{F} = \{\mathbf{f}_\beta, \tau_\beta\}_{\beta=1}^N$ is the applied **forces** and **torques**.
- $k_B T$ is the temperature, and $\mathcal{W}(t)$ is a vector of white noise processes.
- The hydrodynamic **body mobility matrix** $\mathcal{N}(\mathbf{Q}) \succ \mathbf{0}$ is **symmetric and positive-definite**.

I.1 Challenges/Goals

Our group develop novel computational methods for simulating colloidal suspensions that feature:

- Complex shapes: beyond analytical approximations that only work for only spherical particles.
- Boundary conditions: unbounded, periodic, no-slip walls, and in confinement.
- Many-body hydrodynamics: efficient, accurate and scalable to many particles.
- Brownian increments: achieve (near) linear-scaling and strictly obey the **fluctuation-dissipation balance**: $\mathcal{N}^{\frac{1}{2}} \left(\mathcal{N}^{\frac{1}{2}}\right)^* = \mathcal{N}$.
- Stochastic drift: efficient temporal integrators for large-scale simulations.

I.2 Rigid Multiblob Method



(a) Sphere (b) Rod (c) Boomerang

- The rigid body is discretized through a number of "**beads**" or "**blobs**" with prescribed hydrodynamic radius.
- Add **rigidity forces** to constrain a group of blobs to move rigidly.
- Hydrodynamic interactions via **mobility solver**:
  - Unbounded domains: **RPY tensor** with a Fast Multipole Method (FMM).
  - Single wall: **Rotne-Prager-Blake** tensor with **GPU acceleration**.
  - Periodic: **spectral Ewald method** with FFTs.
  - General: **fluid Stokes solver** [1] to compute the **Green's functions on the fly** [3].
- Brownian increments can be efficiently computed in the spectral Ewald or Stokes solver [1] approach using **fluctuating hydrodynamics**.

I.3 Fluctuating Boundary Integral Method (FBIM)

- Only particles' surfaces/boundaries are discretized.
- Hydrodynamics + Brownian increments by solving a **first-kind boundary integral equation (BIE)** with random surface velocity [2].
- Standard techniques for BIE + **Positively Split Ewald** method [5].
- Achieves *linear-scaling* and *controlled accuracy* even for dense suspensions.
- Future work: generalizations to 3D and non-periodic domains.

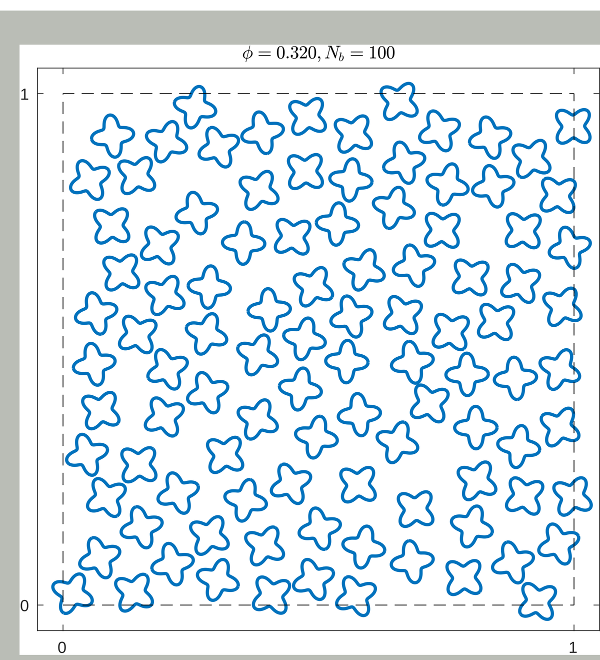
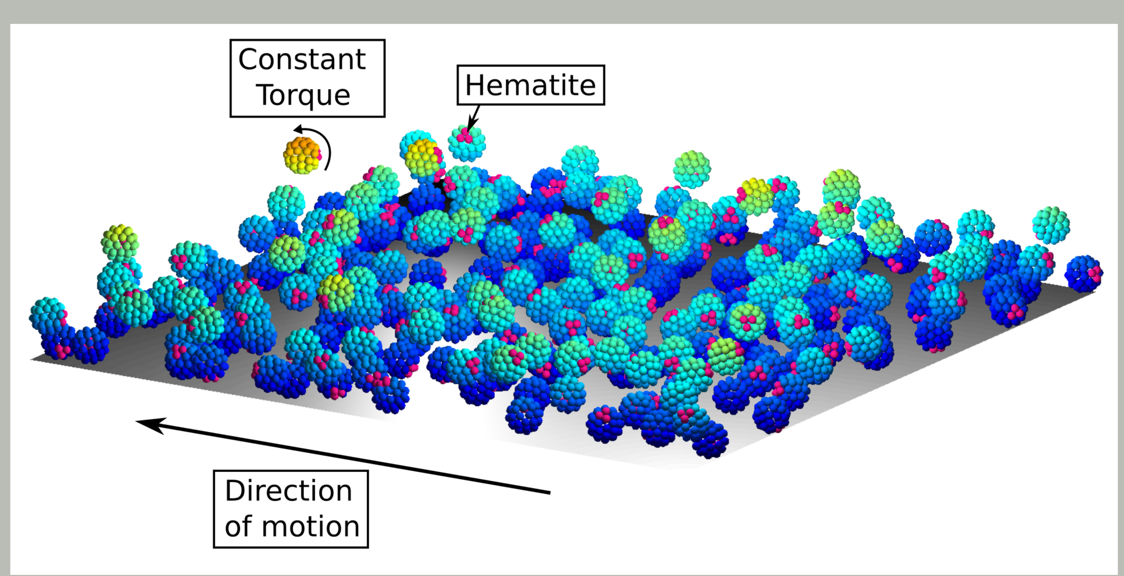


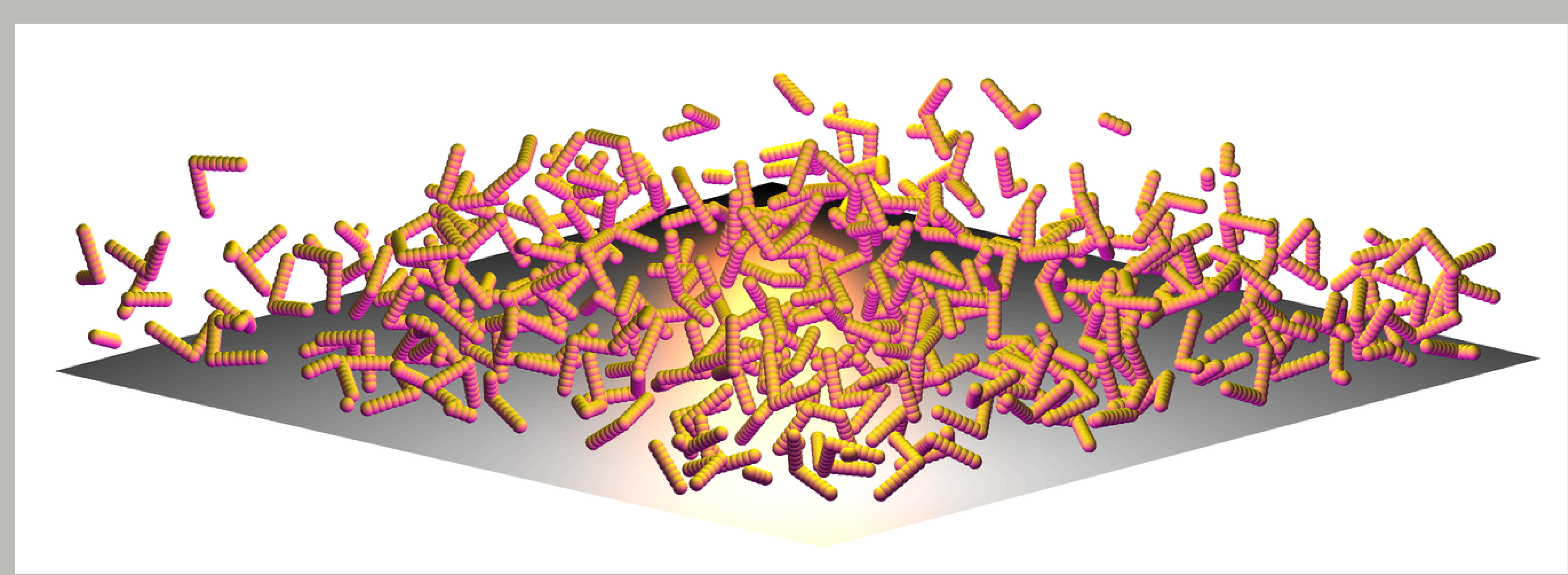
Figure: A colloidal suspension of starfish-shaped particles.

I.4 Large-scale Brownian Dynamics simulations

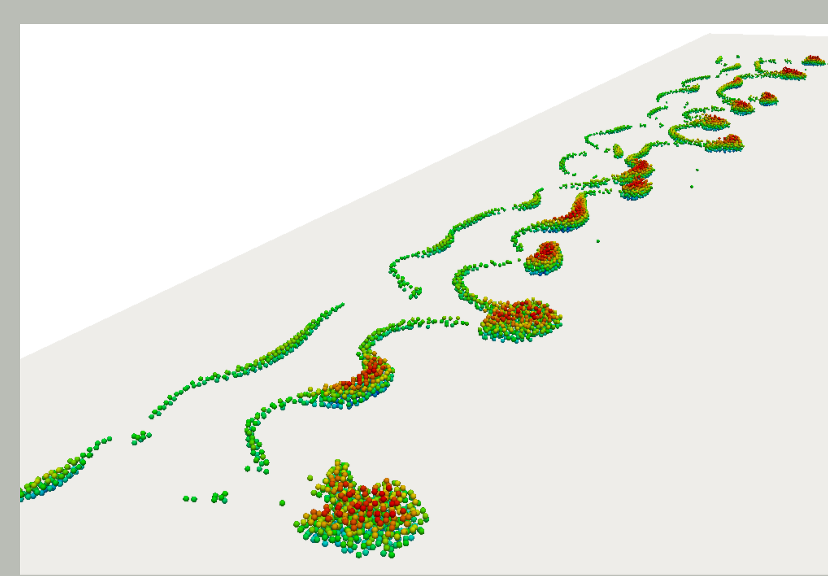
- Developed efficient temporal integrators based on the **Random Finite Difference** [3] technique suitable for large-scale simulations [7, 8].



(a) Translating microrollers



(b) Boomerangs diffusing near wall



(c) Microrollers detach and form critters [4]

PART II. Fluctuating Hydrodynamics of Reactive Electrolyte Mixtures

- Ionic transport in electrolytes (e.g., cell membranes, lithium batteries, fuel cells, etc).
- Classical molecular dynamics are computationally too expensive for the length and time scales involved.
- PI and collaborators at LBNL develop a set of novel models and associated computer algorithms [6] for **fluctuating hydrodynamics** of reactive electrolyte mixtures.

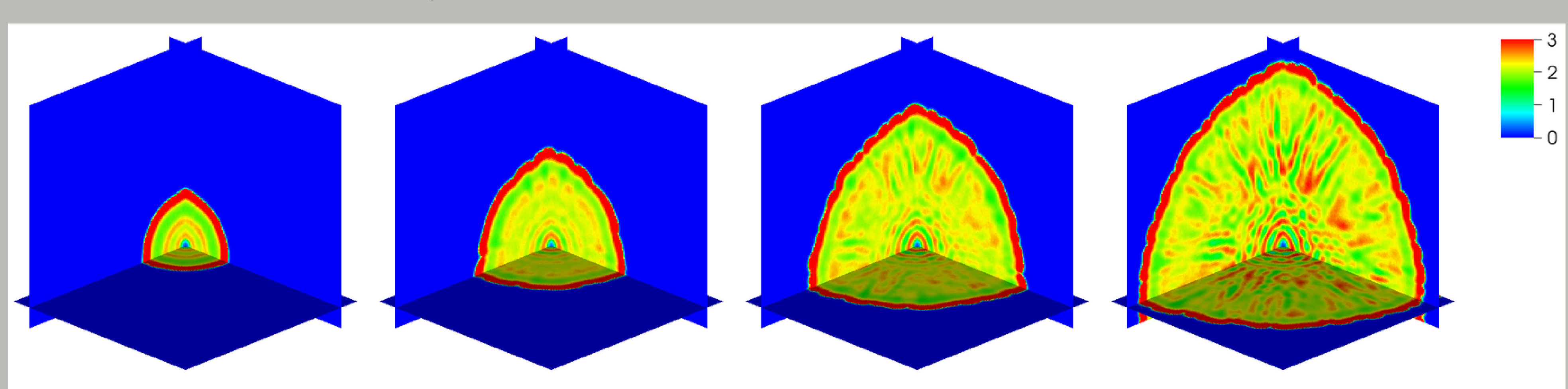


Figure: A traveling wave in a three dimensional solution of active species A and B reacting according to $A \xrightarrow{k_1} \emptyset$, $2A + B \xrightarrow{k_2} 3A$, $\emptyset \underset{k_4}{\overset{k_3}{\rightleftarrows}} B$, starting from a spherically-symmetric initial condition, in the presence of fluctuations. The color scale shows the concentration of A.

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