Rigid Multiblob Methods for Confined Brownian Rigid Particles

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Non-Spherical Colloids near Boundaries

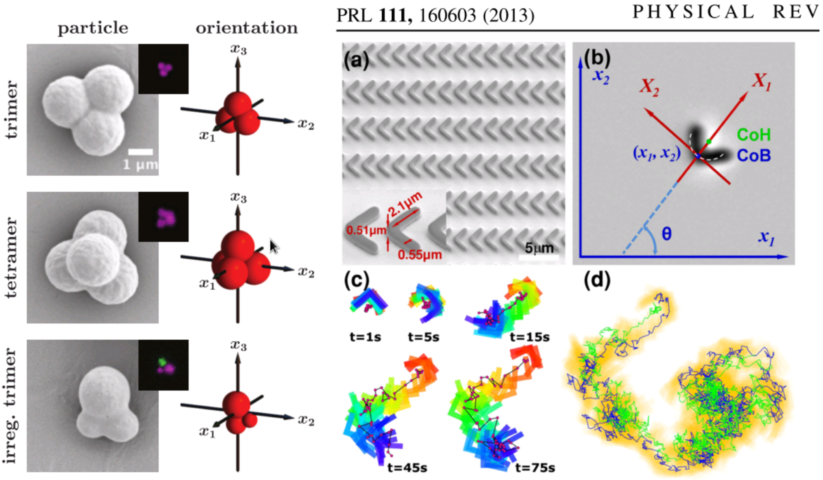


Figure: (Left) Cross-linked spheres; Kraft et al. [1]. (Right) Lithographed boomerangs; Chakrabarty et al. [2].

Bent Active Nanorods

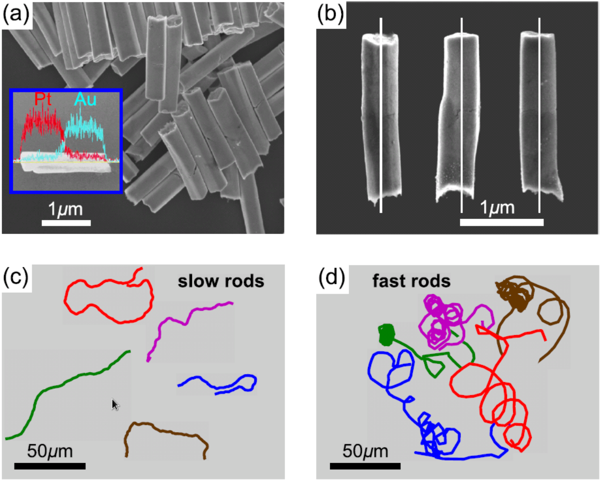
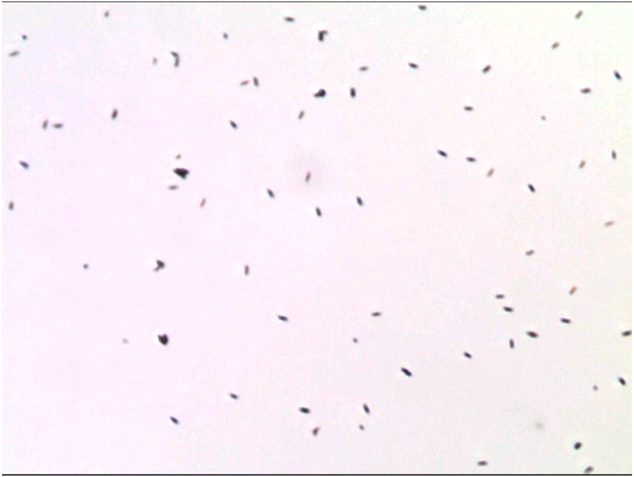


Figure: From the Courant Applied Math Lab of Zhang and Shelley

Thermal Fluctuation Flips



QuickTime

Fluctuating Hydrodynamics

We consider a rigid body Ω immersed in an unbounded fluctuating fluid. In the fluid domain

$$
\begin{aligned}
-\boldsymbol{\nabla}\cdot\boldsymbol{\sigma} = \boldsymbol{\nabla}\pi - \eta\boldsymbol{\nabla}^2\mathbf{v} - (2k_B T\eta)^{\frac{1}{2}}\,\boldsymbol{\nabla}\cdot\boldsymbol{\mathcal{Z}} = 0 \\
\boldsymbol{\nabla}\cdot\mathbf{v} = 0,
\end{aligned}
$$

where the fluid stress tensor

$$
\boldsymbol{\sigma} = -\pi\mathbf{I} + \eta\left(\boldsymbol{\nabla}\mathbf{v} + \boldsymbol{\nabla}^T\mathbf{v}\right) + (2k_B T\eta)^{\frac{1}{2}}\,\boldsymbol{\mathcal{Z}} \tag{1}
$$

consists of the usual **viscous stress** as well as a **stochastic stress** modeled by a symmetric **white-noise** tensor $\boldsymbol{\mathcal{Z}}(\mathbf{r}, t)$, i.e., a Gaussian random field with mean zero and covariance

$$
\left\langle \mathcal{Z}_{ij}(\mathbf{r}, t)\mathcal{Z}_{kl}(\mathbf{r}', t')\right\rangle = \left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}\right)\delta(t - t')\delta(\mathbf{r} - \mathbf{r}').
$$

Fluid-Body Coupling

At the fluid-body interface the **no-slip boundary condition** is assumed to apply,

$$\mathbf{v}(\mathbf{q}) = \mathbf{u} + \mathbf{q} \times \boldsymbol{\omega} \text{ for all } \mathbf{q} \in \partial\Omega, \tag{2}$$

with the **force and torque balance**

$$\int_{\partial\Omega} \boldsymbol{\lambda}(\mathbf{q})\, d\mathbf{q} = \mathbf{F} \quad \text{and} \quad \int_{\partial\Omega} [\mathbf{q} \times \boldsymbol{\lambda}(\mathbf{q})]\, d\mathbf{q} = \boldsymbol{\tau}, \tag{3}$$

where $\boldsymbol{\lambda}(\mathbf{q})$ is the normal component of the stress on the outside of the surface of the body, i.e., the **traction**

$$\boldsymbol{\lambda}(\mathbf{q}) = \boldsymbol{\sigma} \cdot \mathbf{n}(\mathbf{q}).$$

To model activity we can, for example, add **active slip** on the active parts of the surface, or add an **active stress**.

Steady Stokes Flow ($\text{Re} \to 0$)

- Consider a **suspension of N_b rigid bodies** with positions $\mathcal{Q} = \left\{ \boldsymbol{\varrho}_1, \dots, \boldsymbol{\varrho}_{N_b} \right\}$ and orientations $\boldsymbol{\Theta} = \{\boldsymbol{\theta}_1, \dots, \boldsymbol{\theta}_{N_b}\}$.
  We describe orientations using **quaternions**.
- For viscous-dominated flows we can assume **steady Stokes flow** and define the **body mobility matrix** $\mathcal{N}\,(\mathcal{Q}, \boldsymbol{\Theta})$,

$$[\mathcal{U},\, \boldsymbol{\Omega}]^T = \mathcal{N}\,[\mathcal{F},\, \mathcal{T}]^T\,,$$

  where the left-hand side collects the **linear** $\mathcal{U} = \{\boldsymbol{\upsilon}_1, \dots, \boldsymbol{\upsilon}_{N_b}\}$ and **angular** $\boldsymbol{\Omega} = \{\boldsymbol{\omega}_1, \dots, \boldsymbol{\omega}_{N_b}\}$ **velocities**,
  and the right hand side collects the **applied forces** $\mathcal{F}\,(\mathcal{Q}, \boldsymbol{\Theta}) = \{\mathbf{F}_1, \dots, \mathbf{F}_{N_b}\}$ and **torques** $\mathcal{T}\,(\mathcal{Q}, \boldsymbol{\Theta}) = \{\boldsymbol{\tau}_1, \dots, \boldsymbol{\tau}_{N_b}\}$.

Brownian Dynamics

- The Brownian motion of the rigid bodies is described by the **overdamped Langevin equation**, symbolically:

$$\begin{bmatrix} d\mathcal{Q}/dt \\ d\boldsymbol{\Theta}/dt \end{bmatrix} = \begin{bmatrix} \mathcal{U} \\ \boldsymbol{\Omega} \end{bmatrix} = \mathcal{N} \begin{bmatrix} \mathcal{F} \\ \mathcal{T} \end{bmatrix} + \left(2k_B T \mathcal{N}\right)^{\frac{1}{2}} \diamond \mathcal{W}(t) \, .$$

- How to represent orientations using normalized quaternions and handle the constraint $\|\boldsymbol{\Theta}_k\| = 1$?
- What is the correct thermal drift (i.e., what does $\diamond$ mean)?
- **How to compute (the action of) $\mathcal{N}$ and $\mathcal{N}^{\frac{1}{2}}$ and simulate the Brownian motion of the bodies?**

Difficulties/Goals

Stochastic drift It is crucial to handle stochastic calculus issues carefully for **overdamped Langevin** dynamics. Since diffusion is slow we also want to be able to take **large time step sizes**.

Complex shapes We want to stay away from analytical approximations that only work for spherical particles.

Boundary conditions Whenever observed experimentally there are microscope slips (glass plates) that modify the hydrodynamics strongly. It is preferred to use **no Green's functions** but rather work in complex geometry.

Gravity Observe that in all of the examples above there is gravity and the particles sediment toward the bottom wall, often **very close to the wall** ($\sim$ 100nm). This is a general feature of all active suspensions but this is almost always neglected in theoretical models.

Many-body Want to be able to scale the algorithms to suspensions of **many particles**–nontrivial **numerical linear algebra**.

Blob/Bead Models

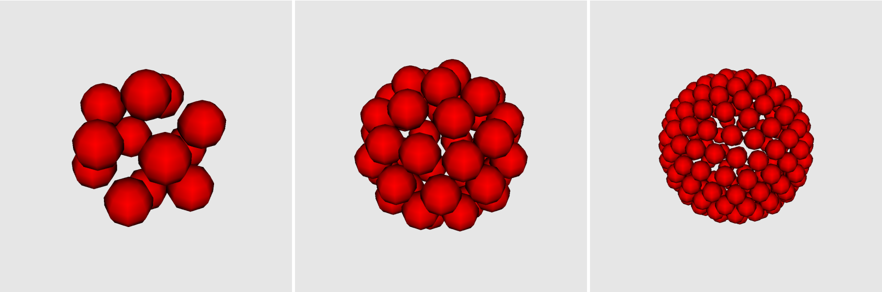


Figure: Blob or "raspberry" models of a spherical colloid.

- The rigid body is discretized through a number of "**beads**" or "**blobs**" with hydrodynamic radius *a*.
- Standard but usually with **stiff springs** instead of **rigid multiblobs**.
- But first let's consider blobs that are free to move relative to one another.

Rigidly-Constrained Blobs

- The **blob-blob mobility matrix** $\mathcal{M}$ describes the hydrodynamic relations between the blobs, accounting for the influence of the boundaries:

$$\mathcal{U} = \mathcal{M}\mathcal{F}$$

- The 3×3 block $\mathbf{M}_{ij}$ maps a force on blob j to a velocity of blob i.
- For well-separated spheres of radius a we have the **Faxen expressions**

$$\mathcal{M}_{ij} \approx \eta^{-1} \left(\mathbf{I} + \frac{a^2}{6} \boldsymbol{\nabla}^2_{\mathbf{r}} \right) \left(\mathbf{I} + \frac{a^2}{6} \boldsymbol{\nabla}^2_{\mathbf{r}'} \right) \mathbf{G}(\mathbf{r} - \mathbf{r}') \Big|^{\mathbf{r}=\mathbf{q}_j}_{\mathbf{r}'=\mathbf{q}_i}$$

  where $\mathbf{G}$ is the Green's function (**Oseen tensor** for unbounded).
- This gives the well-known **Rotne-Prager-Yamakawa tensor** for the mobility of pairs of blobs.

Rigidly-Constrained Blobs

- We add **rigidity forces** as Lagrange multipliers $\boldsymbol{\lambda} = \{\boldsymbol{\lambda}_1, \ldots, \boldsymbol{\lambda}_n\}$ to constrain a group of blobs to move rigidly,

$$\begin{aligned} \sum_j \mathbf{M}_{ij}\boldsymbol{\lambda}_j =& \mathbf{u} + \boldsymbol{\omega} \times (\mathbf{r}_i - \mathbf{q}), \quad \forall i \\ \sum_i \boldsymbol{\lambda}_i =& \mathbf{F} \\ \sum_i (\mathbf{r}_i - \mathbf{q}) \times \boldsymbol{\lambda}_i =& \boldsymbol{\tau}, \end{aligned} \tag{4}$$

  where $\mathbf{u}$ is the velocity of the tracking point $\mathbf{q}$, $\boldsymbol{\omega}$ is the angular velocity of the body around $\mathbf{q}$, $\mathbf{F}$ is the total force applied on the body, $\boldsymbol{\tau}$ is the total torque applied to the body about point $\mathbf{q}$, and $\mathbf{r}_i$ is the position of blob i.
- This can be a very large linear system for suspensions of many bodies discretized with many blobs: **iterative solvers** that require a **good preconditioner**.

Suspensions of Rigid Bodies

- In matrix notation we have a linear system of equations for the rigidity forces $\boldsymbol{\Lambda}$ and unknown motion $\boldsymbol{\mathcal{Y}}$,

$$\boldsymbol{\mathcal{M}}\boldsymbol{\Lambda} = \boldsymbol{\mathcal{K}}\boldsymbol{\mathcal{Y}} + \text{slip}$$
$$\boldsymbol{\mathcal{K}}^{\star}\boldsymbol{\Lambda} = \boldsymbol{\mathcal{R}},$$

  where the unknown $\boldsymbol{\mathcal{Y}} = [\boldsymbol{\mathcal{U}}, \boldsymbol{\Omega}]^{T}$ are the body kinematics, $\boldsymbol{\mathcal{R}} = [\boldsymbol{\mathcal{F}}, \boldsymbol{\mathcal{T}}]^{T}$ are the applied forces and torques.

- Taking the Schur complement of the linear system we get

$$\boldsymbol{\mathcal{Y}} = \begin{bmatrix} \boldsymbol{\mathcal{U}} \\ \boldsymbol{\Omega} \end{bmatrix} = \boldsymbol{\mathcal{N}}\boldsymbol{\mathcal{R}} = \boldsymbol{\mathcal{N}} \begin{bmatrix} \boldsymbol{\mathcal{F}} \\ \boldsymbol{\mathcal{T}} \end{bmatrix} + \text{slip terms.}$$

- The **many-body mobility matrix** $\boldsymbol{\mathcal{N}}$ takes into account **rigidity** and higher-order **hydrodynamic interactions**,

$$\boldsymbol{\mathcal{N}} = \left(\boldsymbol{\mathcal{K}}^{\star}\boldsymbol{\mathcal{M}}^{-1}\boldsymbol{\mathcal{K}}\right)^{-1}.$$

How to Approximate the Mobility

- In order to make this method work we need a way to compute the (action of the) blob-blob mobility $\mathcal{M}$.
- There are different ways to obtain $\mathcal{M}$:
  - In unbounded domains we can just use the **Rotne-Prager-Yamakawa tensor** (RPY) (always SPD!).
  - In simple geometries such as a single wall we can use a **generalization of RPY** [3].
  - For periodic domains we can use Ewald-type summations or **non-uniform FFTs** with a fluctuating **spectral fluid solver** [4].
  - In more general cases we can use a fluctuating **FEM/FVM fluid Stokes solver** [5]:
    Brownian Dynamics without Green's functions! [6]
    In the grid-based approach adding thermal fluctuations (Brownian motion) can be done using **fluctuating hydrodynamics**.

Bodies with rotation

- We can extend our work to simulate bodies with **rotational DOFs** by formulating the appropriate Langevin equation and using a RFD approach to for temporal integration.
- For simplicity, first we consider a single body with only rotational degrees of freedom.
- Orientation is an element of SO(3) so we need to parameterize it: we use **normalized quaternion** (point on the unit 4-sphere)

$$\boldsymbol{\theta} \in \mathbb{R}^4, \quad \|\boldsymbol{\theta}\|_2 = \boldsymbol{\theta} \cdot \boldsymbol{\theta} = 1.$$

- This offers several advantages over several other common approaches, such as rotation angles, rotation matrices, and Euler angles.

Quaternions

- Successive rotations can be accumulated by **quaternion multiplication.**
- In three dimensions, there exists a 4×3 matrix $\boldsymbol{\Psi}(\boldsymbol{\theta})$ such that, given a conservative potential $U(\boldsymbol{\theta})$,

$$\dot{\boldsymbol{\theta}} = \boldsymbol{\Psi}\boldsymbol{\omega}, \quad \boldsymbol{\tau} = \boldsymbol{\Psi}^T \partial_{\boldsymbol{\theta}} U(\boldsymbol{\theta}).$$

  Here $\boldsymbol{\tau}$ is the torque applied to the body, and $\boldsymbol{\omega}$ is the angular velocity.
- One can also rotate a body by an oriented angle ϕ, denoted as

$$\boldsymbol{\theta}^{n+1} = \text{Rotate}\left(\boldsymbol{\theta}^n, \, \phi\right).$$

Equations for Rotation

- We assume now that we know the mobility tensor $\mathbf{M}_{\boldsymbol{\omega}\boldsymbol{\tau}}$,

$$\boldsymbol{\omega} = \mathbf{M}_{\boldsymbol{\omega}\boldsymbol{\tau}} \boldsymbol{\tau}.$$

- Given $\mathbf{M}_{\boldsymbol{\omega}\boldsymbol{\tau}}$ and a potential $U(\boldsymbol{\theta})$, the **Overdamped Langevin Equation** for orientation is

$$\begin{aligned} \partial_t \boldsymbol{\theta} = & - \left(\boldsymbol{\Psi} \mathbf{M}_{\boldsymbol{\omega}\boldsymbol{\tau}} \boldsymbol{\Psi}^T \right) \partial_{\boldsymbol{\theta}} U + \sqrt{2 k_B T} \boldsymbol{\Psi} \mathbf{M}_{\boldsymbol{\omega}\boldsymbol{\tau}}^{\frac{1}{2}} \boldsymbol{\mathcal{W}} \\ & + k_B T \partial_{\boldsymbol{\theta}} \cdot \left(\boldsymbol{\Psi} \mathbf{M}_{\boldsymbol{\omega}\boldsymbol{\tau}} \boldsymbol{\Psi}^T \right). \end{aligned}$$

- This equation preserves the unit norm constraint and is time reversible w.r.t. the **Gibbs-Boltzmann distribution**

$$P_{\text{eq}} \left(\boldsymbol{\theta} \right) = Z^{-1} \exp \left(-U \left(\boldsymbol{\theta} \right) / k_B T \right) \delta \left(\boldsymbol{\theta}^T \boldsymbol{\theta} - 1 \right).$$

Algorithm with Translation

- To include translation, we introduce the matrix $\boldsymbol{\Xi}$, letting $\mathbf{u} = \dot{\mathbf{q}}$ where $\mathbf{q}$ is the location of the body,

$$\boldsymbol{\Xi} = \begin{bmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\Psi} \end{bmatrix}, \quad \left[\dot{\mathbf{q}}, \dot{\boldsymbol{\theta}}\right]^T = \boldsymbol{\Xi}\left[\mathbf{u}, \omega\right]^T$$

- The complete **overdamped Langevin equations** are

$$\begin{bmatrix} \mathbf{u} \\ \dot{\boldsymbol{\theta}} \end{bmatrix} = -\left(\boldsymbol{\Xi}\mathcal{N}\boldsymbol{\Xi}^{\star}\right)\begin{bmatrix} \partial_{\mathbf{q}} U \\ \partial_{\boldsymbol{\theta}} U \end{bmatrix} + \sqrt{2k_B T}\,\boldsymbol{\Xi}\mathbf{N}^{\frac{1}{2}}\mathcal{W} + (k_B T)\,\partial_{\mathbf{x}} \cdot \left(\boldsymbol{\Xi}\mathbf{N}\boldsymbol{\Xi}^{\star}\right)$$

- We have developed specialized **temporal integrators** to solve these equations efficiently for confined bodies [7].

Random Finite Difference

- To take a time step in a **Brownian Dynamics** algorithm with rotational diffusion we do:

$$\begin{aligned}
\tilde{\mathbf{v}} =& \widetilde{\mathbf{W}} \\
\tilde{\mathbf{q}} =& \mathbf{q}^n + \delta \tilde{\mathbf{u}} \\
\tilde{\boldsymbol{\theta}} =& \text{Rotate}\left(\boldsymbol{\theta}^n, \delta \tilde{\boldsymbol{\omega}}\right) \\
\mathbf{v}^n =& -\left(\mathbf{N}\boldsymbol{\Xi}^T \partial_{\mathbf{x}} U\right)^n + \sqrt{\frac{2k_B T}{\Delta t}} \left(\mathbf{N}^{\frac{1}{2}}\right)^n \mathbf{W}^n + \frac{k_B T}{\delta} \left(\widetilde{\mathbf{N}} - \mathbf{N}^n\right) \widetilde{\mathbf{W}} \\
\mathbf{q}^{n+1} =& \mathbf{q}^n + \Delta t \mathbf{u}^n \\
\boldsymbol{\theta}^{n+1} =& \text{Rotate}\left(\boldsymbol{\theta}^n, \Delta t \boldsymbol{\omega}^n\right).
\end{aligned}$$

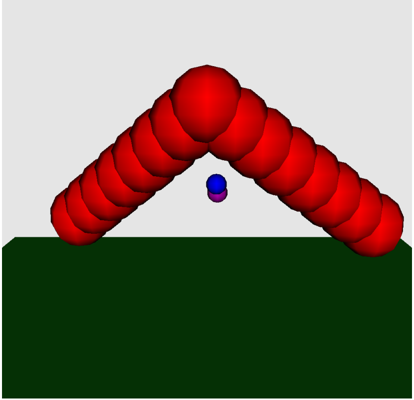
Brownian motion under gravity

- We consider the Brownian motion of a single rigid body near a no-slip boundary.
- Temporal integration of the overdamped equations is done using a **random finite different (RFD)**.
- Number of blobs is small and we have a simple geometry so we use approximate **Blake-Rotne-Prager tensor** (Brady & Swan [3])
- For this test we use **direct linear algebra** to compute $\mathcal{N}$ and Cholesky factorization to compute $\mathcal{N}^{\frac{1}{2}}$.
- We add gravity which makes the equilibrium **Gibbs-Boltzmann distribution** be

$$P_{GB}(\mathcal{Q}, \boldsymbol{\Theta}) \sim \exp\left[-\frac{mgh + U_{\text{steric}}}{k_B T}\right],$$

where h is the center-of-mass height and U_{steric} is a Yukawa-type repulsion with the wall.

Diffusion of a Confined Boomerang



Quasi-2D ($g = 20$)

Translational+Rotational Diffusion

- We define the total **mean square displacement** (MSD) at time τ

$$\mathbf{D}(\tau;\mathbf{x}) = \langle \Delta\mathbf{X}(\tau;\mathbf{x}) \left(\Delta\mathbf{X}(\tau;\mathbf{x})\right)^T \rangle, \tag{5}$$

where $\Delta X(\tau;\mathbf{x}) = (\Delta\mathbf{q}(\tau;\mathbf{x}),\, \Delta\hat{\mathbf{u}}(\tau;\mathbf{x}))$, with orientation increment $\Delta\hat{\mathbf{u}}(\tau)$ [1]

$$\Delta\hat{\mathbf{u}}\left(\Delta t\right) \equiv \frac{1}{2}\sum_{i=1}^{3} \mathbf{u}_i(0) \times \mathbf{u}_i\left(\Delta t\right). \tag{6}$$

- The **Stokes-Einstein relation** gives the **short-time** mean square displacement,

$$\chi_{st} = \frac{1}{2}\lim_{\tau\to 0} \frac{\langle \mathbf{D}_{\text{trans}}(\tau;\mathbf{x}) \rangle}{\tau} = k_B T \left\langle \mathbf{M}_{\mathbf{uF}}\left(\mathbf{x}\right) \right\rangle. \tag{7}$$

- In general, it is much harder to characterize the **long-time** diffusion coefficient

$$\chi_{lt} = \frac{1}{2}\lim_{\tau\to\infty} \frac{\langle \mathbf{D}_{\text{trans}}(\tau;\mathbf{x}) \rangle}{\tau} \tag{8}$$

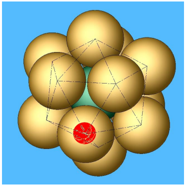
Quasi-2D Diffusion

- Brownian motion is confined near the bottom wall so it **quasi-two dimensional**.
- Without external forcing the Brownian motion along the wall should be isotropic diffusive at long time scales.
- A naive guess for the **effective 2D diffusion coefficient** would be the Gibbs-Boltzmann average of the parallel translational mobility:

$$D_{\parallel} = k_B T \left\langle \mu_{\parallel} \right\rangle_{\text{GB}} .$$

- This is in fact a theorem for a sphere because rotational Brownian motion does not change the mobility.
  Is it true for non-spherical particles?

MSD for a sphere



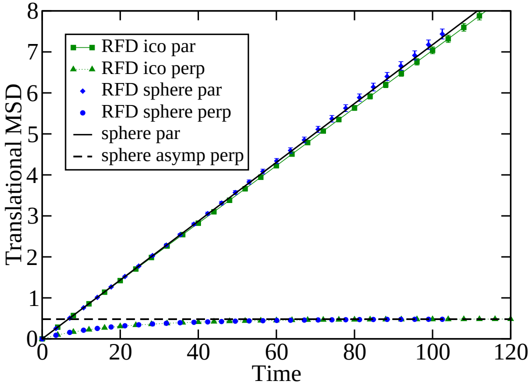
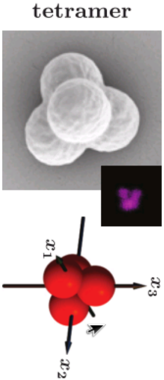


Figure: Mean square displacement (MSD) for a non-uniform **spherical particle** of unit diameter discretized as an icosahedron of 12 blobs or just a single blob.

The choice of tracking point matters



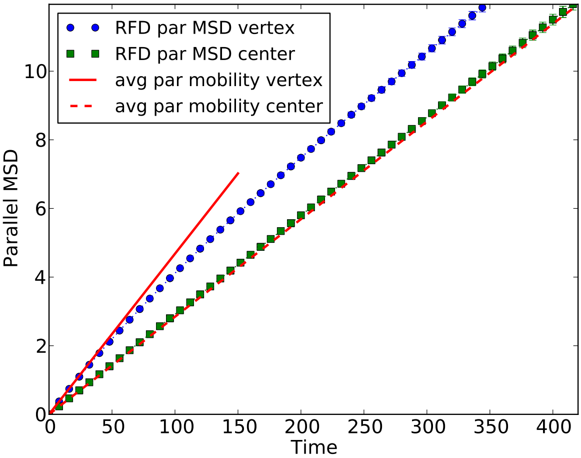


Figure: MSD for a **non-spherical particle** (tetrahedron/tetramer).

Tracking Point

- We want the translational MSD to be **strictly linear in time** so that the long and short time diffusion coefficients are equal.
- Does there exist a choice of tracking point that makes the MSD linear in time? (No!)
- But some candidates for a **better** choice of tracking point exist.
- For any body shape and **specific position relative to the boundary**, there exists a unique point in the body called the **center of mobility** (CoM) that makes the coupling tensors symmetric,

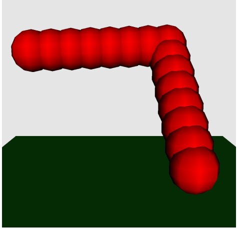
$$\mathbf{M}_{\omega\mathbf{F}}^{T} = \mathbf{M}_{\omega\mathbf{F}} = \mathbf{M}_{\mathbf{u}\boldsymbol{\tau}} = \mathbf{M}_{\mathbf{u}\boldsymbol{\tau}}^{T}.$$

  This is the best tracking point for **isotropic (bulk) diffusion**.
- For some bodies of sufficient symmetry, there exists a point called the **center of hydrodynamic stress** (CoH), where the cross-coupling vanishes,

$$\mathbf{M}_{\omega\mathbf{F}} = \mathbf{M}_{\mathbf{u}\boldsymbol{\tau}} = 0.$$

  Track an approximate CoH for quasi-2D diffusion [2]?

Boomerangs: Translation



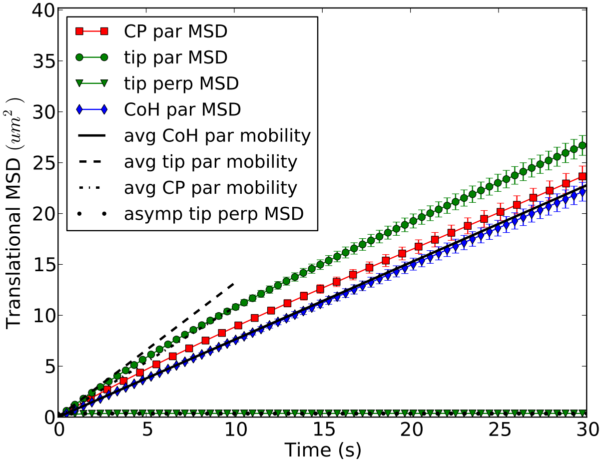
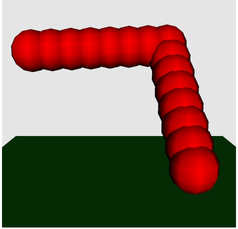


Figure: Translational MSD for a boomerang

Boomerangs: Rotation



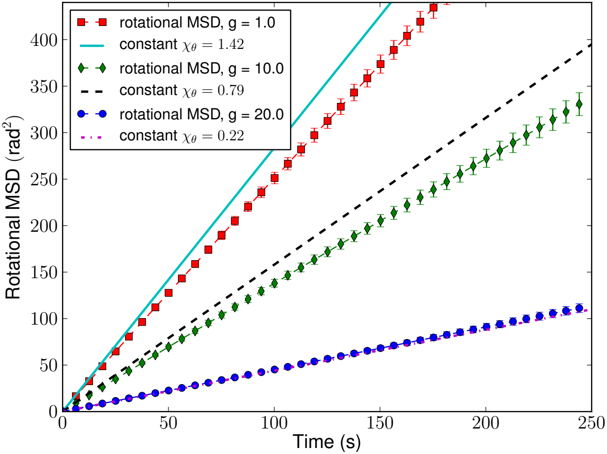


Figure: Rotational MSD for a boomerang

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