Self-propulsion of active symmetric and asymmetric nanomotors

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17 December 2014

http://fys.kuleuven.be/itf/
http://pdebuyl.be/

Outline

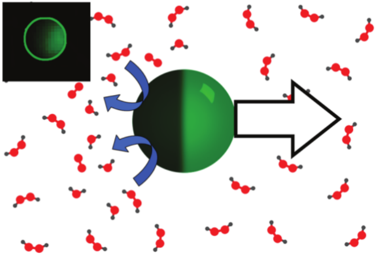
Outline

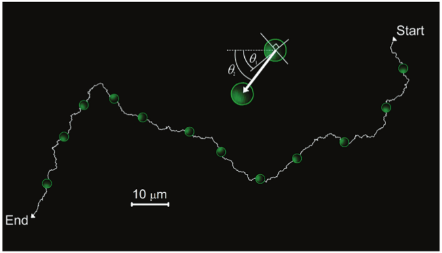
Acknowledgments & links

- Work done with R. Kapral (Toronto, all) and A. S. Mikhailov (Berlin, symmetric motor) while at the University of Toronto and the Université libre de Bruxelles

- Slides on my website `http://pdebuyl.be/`, all references and links clickable

The "typical" motor





- Ebbens & Howse, Langmuir **27** 12293 (2011) doi:10.1021/la2033127
- Scale $\approx 1\mu$m

A small motor

- Lee *et al* Nano Letters **14** 2407 (2014) doi:10.1021/nl500068n
- Scale ≈ 30nm

Other motors

- Rotors
- Conformational changes in enzymes
- Pumps: fix the motor, the fluid moves

Active colloids

- **Features:**
  - Chemical activity on the surface
  - Significant thermal motion
- **Nanomotor & self-propulsion**:
  - Device that converts a fuel into work
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- **Features:**
  - Chemical activity on the surface
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- **Nanomotor & self-propulsion**:
  - Device that converts a fuel into work
  - Origin of motion (gradient) generated locally
- Interesting statistical physics devices
- Many similarities with biological behaviour: use of neigbouring fuel, strong thermal fluctuations, similar length-scales (ηm-μm)

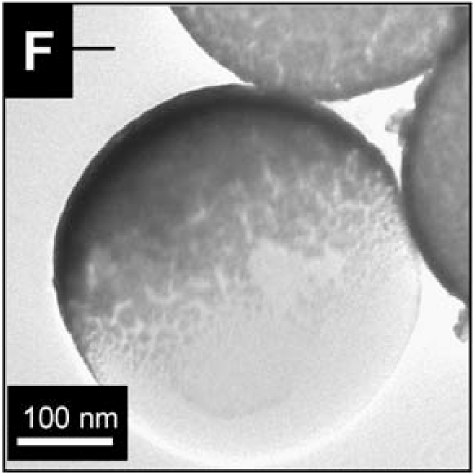
The Janus particle

- The two-faced roman god Janus gave his name to asymmetrical colloidal compounds
- The two sides are translated into different chemical activities

Credit: WikiPedia user Fubar Obfusco link

The Janus particle - reality

- It is possible to make micron and sub-micron sized Janus particles
- The one presented here is coated with Au, but the typical self-propelled particle is coated with Pt



Credit: Suzuki and Kawaguchi, Colloid Polym. Sci. **284**, 1471 (2006). doi:10.1007/s00396-006-1524-5

The Janus particle - reality (...)

- Self-propelled Janus particles have been realized experimentally
- Top: Howse *et al*, Phys. Rev. Lett. (2007) link
- Bottom: Ke *et al*. J. Phys. Chem. A (2010) link

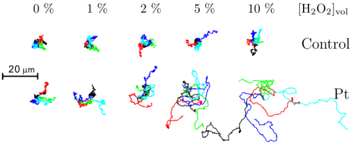
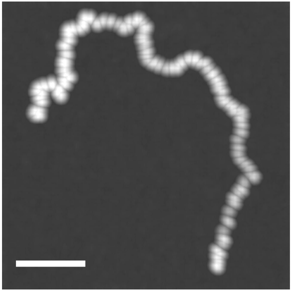
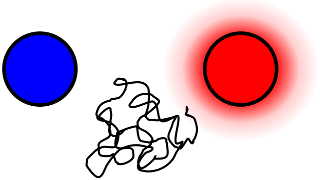


FIG. 1 (color online). Trajectories over 25 sec for ×5 particles of the control (blank) and platinum-coated particles in water and varying solutions of hydrogen peroxide.



Operation of active colloids



- Blue = passive Red = active

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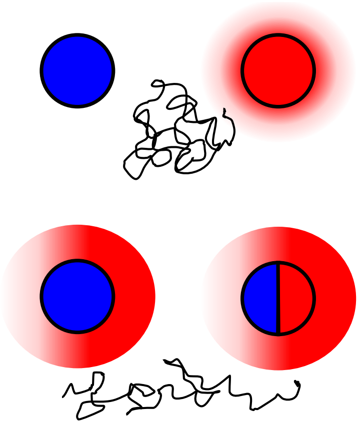

- Blue = passive   Red = active
- Functionalize specific sites of a colloid
- Asymmetry → gradient generation
- → self-propulsion
- Basic operation of a chemical engine

Outline

Modeling of the Janus particle

- Objective: get a tractable computer model for active colloids
- Building block:
  - The colloid is made up of beads, rigidly maintained into an arbitrary shape
  - The colloid evolves by molecular dynamics (MD)
  - The beads making up the colloid can be either chemically active or not

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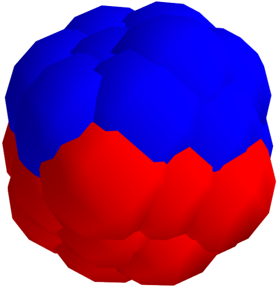

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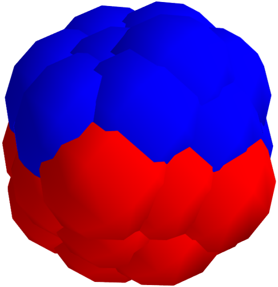

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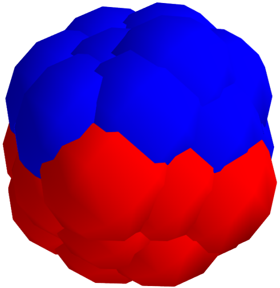
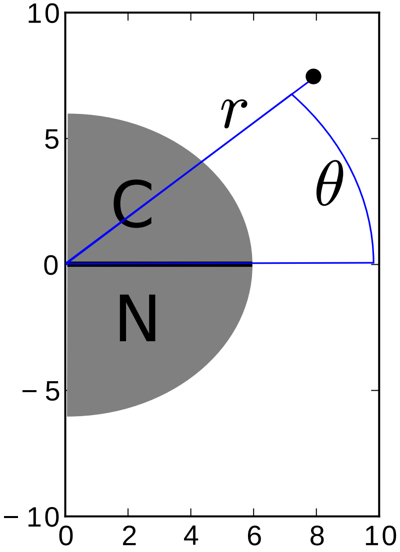
  - The method combines structure and function
  - The methodology can be extended to other shapes, to elastic networks, etc

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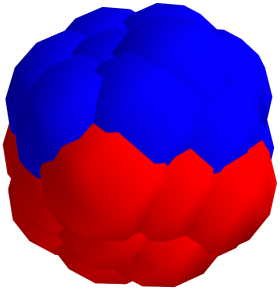
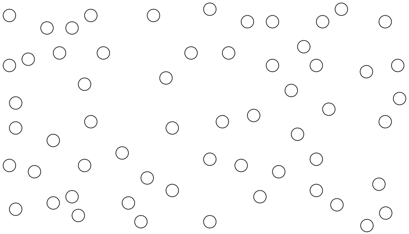


Solvent modeling: the MPCD Algorithm

- An ensemble of point particles is evolved in two steps:
  - Stream at constant velocity: $x^{t+1} = x^t + v^t \Delta t$
  - Cell-wise collision



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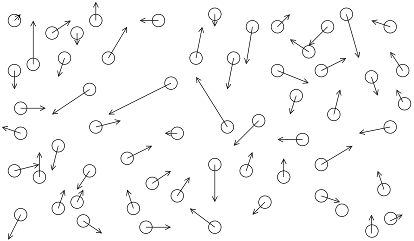

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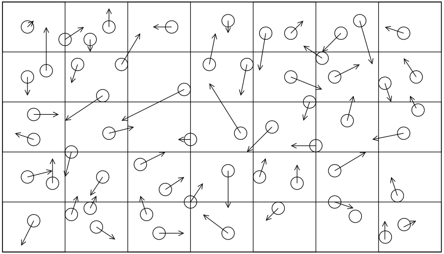

MPCD Algorithm - key properties

- Conservation of
  - mass
  - momentum
  - energy
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- Conservation of
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- Considerably cheaper than full MD
- Solvent within interaction range of a colloid evolve according to MD

Algorithm - coupling to MD

- Inside the fluid solvent, we include Lennard-Jones (LJ) particles
- These particles interact via a repulsive LJ: truncation at $r = 2^{1/6}\sigma$
- Different ϵ for the combinations of $(A,B)\times(C,N)$ lead to phoretic effects

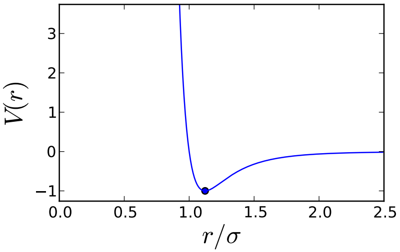

Figure: The repulsive LJ potential is cut at the bottom of the well.

$$H_{LJ} = 4\epsilon \sum_{i,j} \left((\frac{\sigma}{r_{ij}})^{12} - (\frac{\sigma}{r_{ij}})^{6} + \frac{1}{4} \right)$$

The sum is between solvent particles and solute particles with $r_{ij} \leq 2^{1/6}\sigma$

Modeling (re)active colloids

- An active colloid $\rightarrow$ a colloid that modifies the properties of the surrounding fluid
- Can be chemical or thermal, for instance
- Ability
  - to use fuel from the environment
  - to generate local gradients

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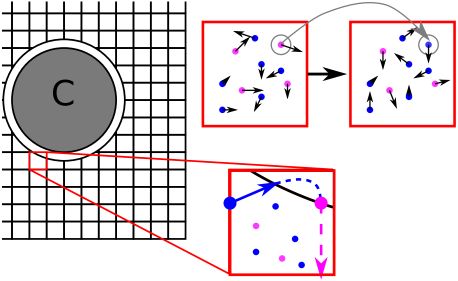
- An active colloid $\rightarrow$ a colloid that modifies the properties of the surrounding fluid
- Can be chemical or thermal, for instance
- Ability
  - to use fuel from the environment
  - to generate local gradients
- Modeling active colloids requires the inclusion of chemical activity in the simulation model

Modeling of reactive events

- Encounters of solvent particles with the colloid triggers a reactive event
- Events occur upon leaving the interfacial (or interaction) boundary of the colloid
- Bulk reaction are also considered, within the MPCD collision steps



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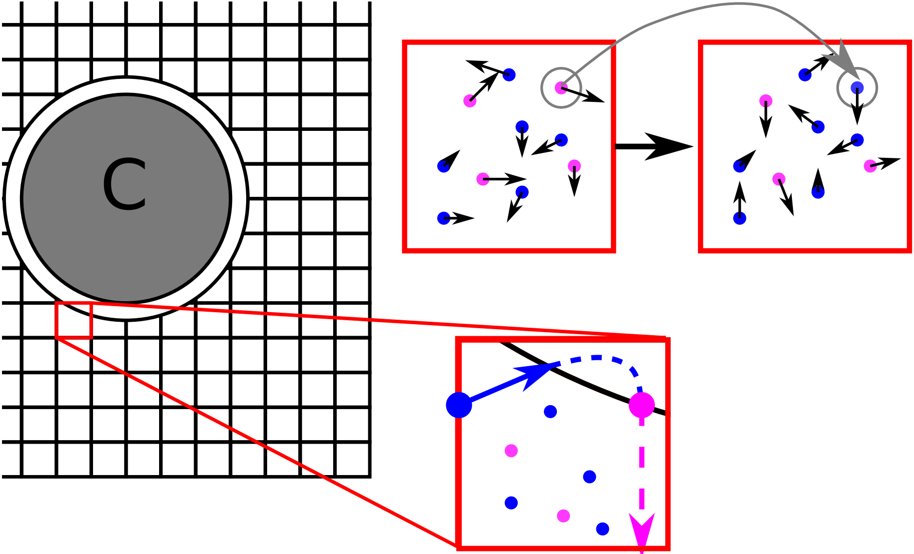

Outline

"Experimental setting"

- Janus particle half-coated by "C", triggering reactive events

$$A + C \to B + C$$

- Potential of B can be modified with respect to A
- "Far away", $B \to A$ in the bulk

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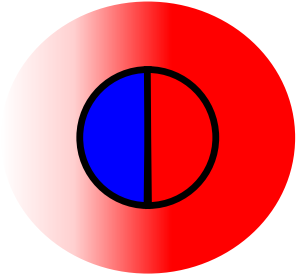
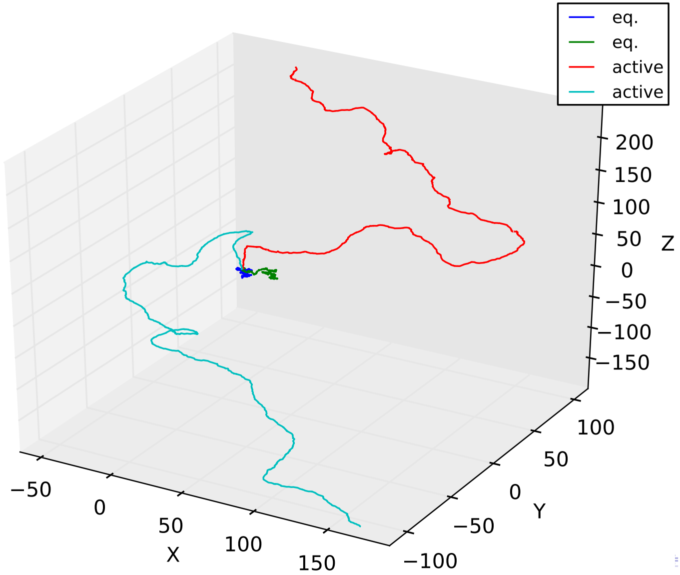


Reactive simulations

The Janus particle with a chemical reaction

Self-propulsion



Self-propulsion

- Let us define the directed velocity V_z

$$V_z(t) = \frac{1}{t} \int_0^t dt' \, \mathbf{r}_{CN}(t') \cdot \mathbf{v}(t') \qquad (1)$$

$\langle V_z \rangle(t)$ is $V_z(t)$ averaged over 16 simulation runs

Self-propulsion

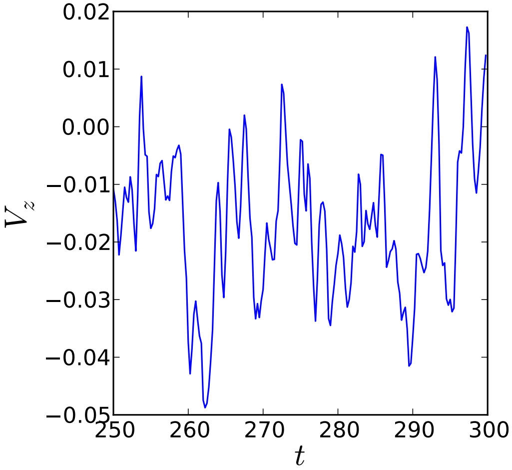


Figure: The directed velocity of the Janus particle.

Self-propulsion

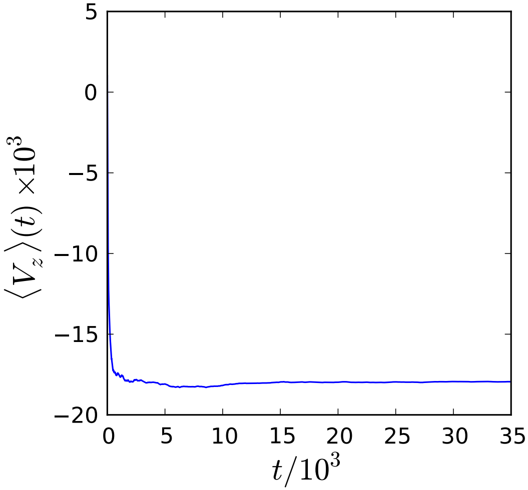


Figure: Running average of the directed velocity of the Janus particle.

Self-propulsion

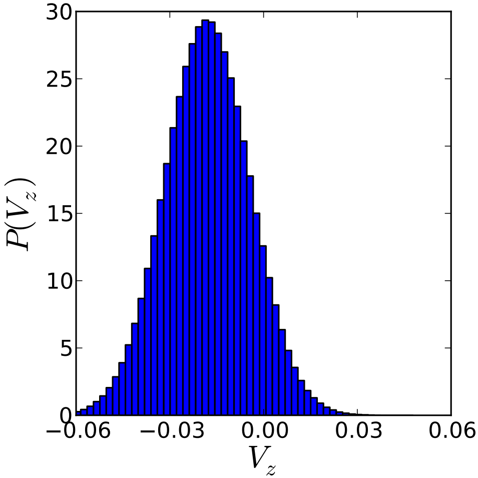
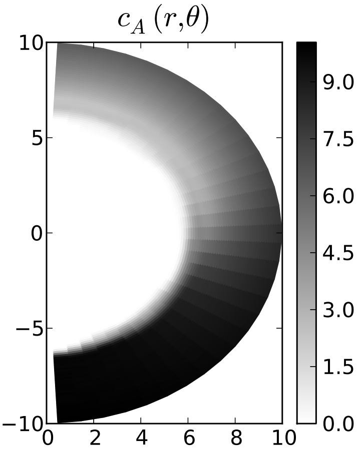
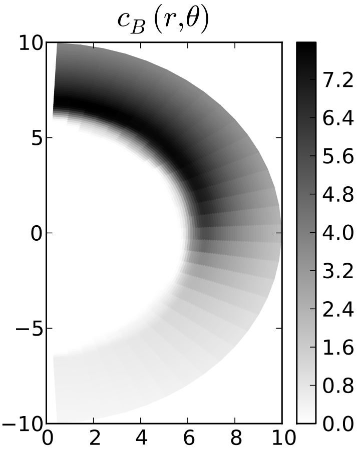


Figure: The directed velocity distribution for the Janus particle.

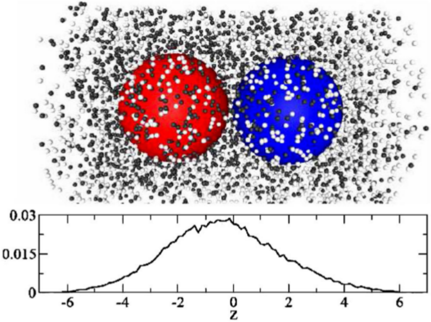
Self-propulsion





Self-propulsion

- For now, our results follow the idea of the dimer nanomotor studied by Rückner & Kapral, PRL **98** 150603 (2007) doi:10.1103/PhysRevLett.98.150603



Outline

Phoretic schemes

- *Old* simulations: thermoneutral unimolecular reactions
- *New* schemes conserve momentum and energy
- Change the nature of the self-generated gradient
- We have implemented two simple chemical processes
  - An exothermic reaction $A + C \to B + C + \Delta u$
  - A dissociation reaction $A + C \to 2B + C$
- In the following, refueling is performed as a bulk reaction with a small rate

Phoretic schemes

- As opposed to the "coloring" $A + C \to B + C$ reaction, the exothermic and dissociation reactions cannot satisfy conservation rule
- To restore the conservation property, additional solvent particles are involved
- Momentum:

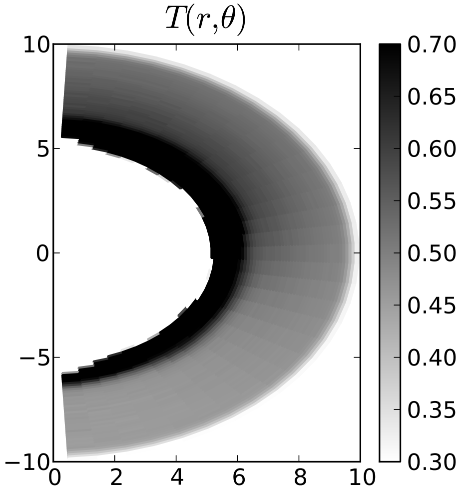
$$m_J \mathbf{v}_J + \sum_{i \in \xi} m_i \mathbf{v}_i = m_J \mathbf{v}'_J + \sum_{i \in \xi} m_i \mathbf{v}'_i$$

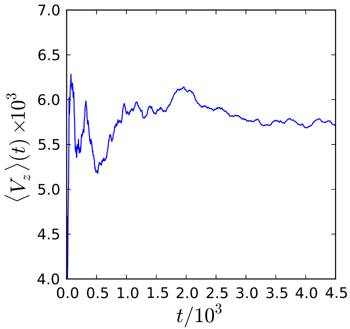
- Energy:

$$\frac{1}{2} m_J \mathbf{v}_J^2 + \frac{1}{2} \sum_{i \in \xi} m_i \mathbf{v}_i^2 + \sum_{i \in \xi} u_i = \frac{1}{2} m_J \mathbf{v}_J'^2 + \frac{1}{2} \sum_{i \in \xi} m_i \mathbf{v}_i'^2 + \sum_{i \in \xi} u'_i$$

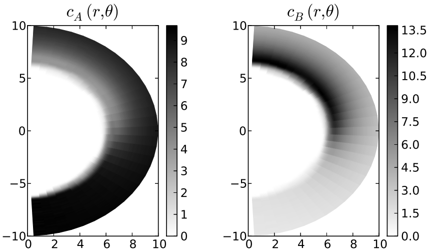
- $\mathbf{v}_J$ and $\mathbf{v}_i$ are the velocities of the Janus particle and a solvent particle, m_J and m_i are masses, α the chemical species (with internal energy u_α)

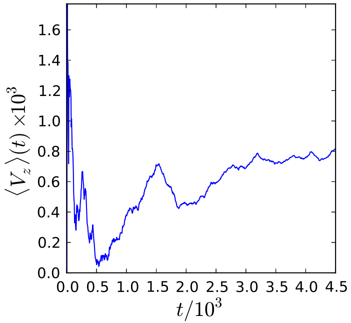
Exothermic reaction





Dissociation reaction





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Setup for a single active sphere

- A single active spherical colloid
- The sphere converts the A species of the fluid into the B species
- As for the Janus particle, a key point is that the interaction between the A and B species and the colloid is different

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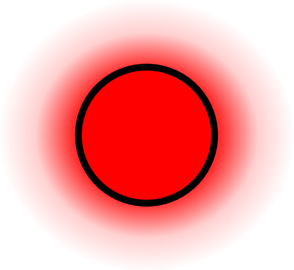
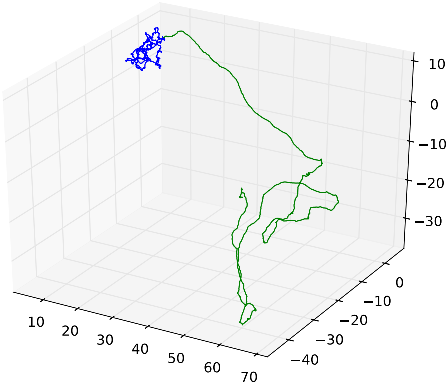


Equilibrium and active trajectories



Dynamics of the active colloid

The departure of the dynamics from an equilibrium situation is tracked by the following quantities:

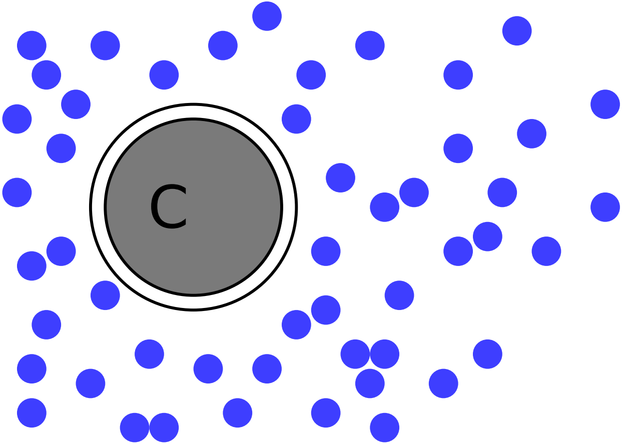
- The average speed $\langle V' \rangle$
- The distribution for the speed (norm of the velocity): $P(V')$
- The Mean Squared Displacement (MSD)

All speeds V' are scaled by the thermal velocity $\sqrt{\frac{k_B T}{M}}$, where M is the mass of the colloid

Setup

- We consider identical systems with varying sphere radii from $\sigma = 3$ to $\sigma = 9$
- Simulations are compared to non-reactive runs and results are taken from an average over realizations
- The B fluid species (magenta) is more repulsive than the A species (blue)

Principle of operation



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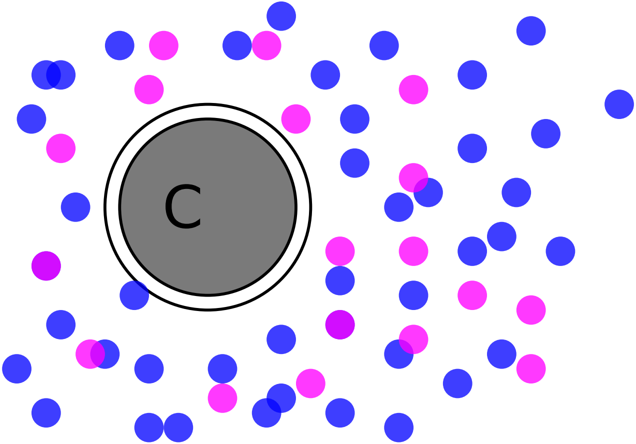

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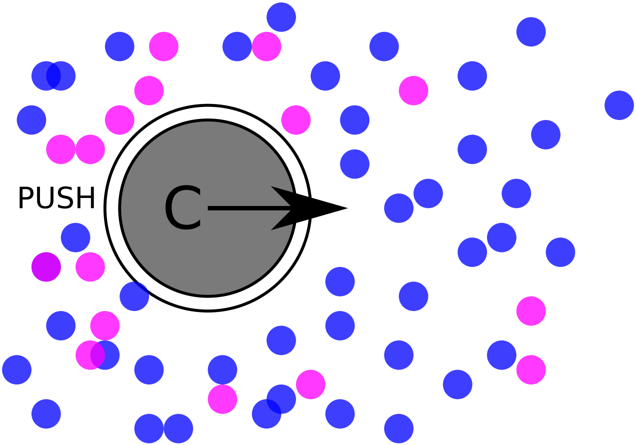
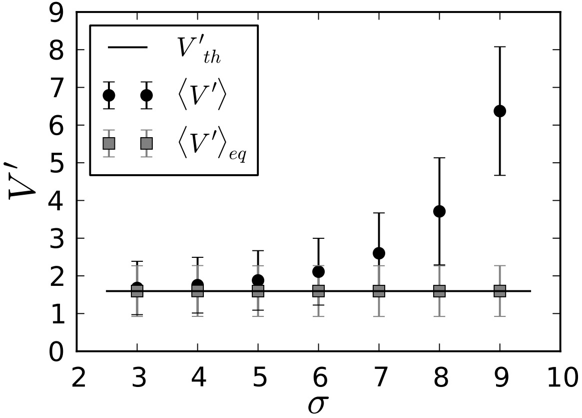
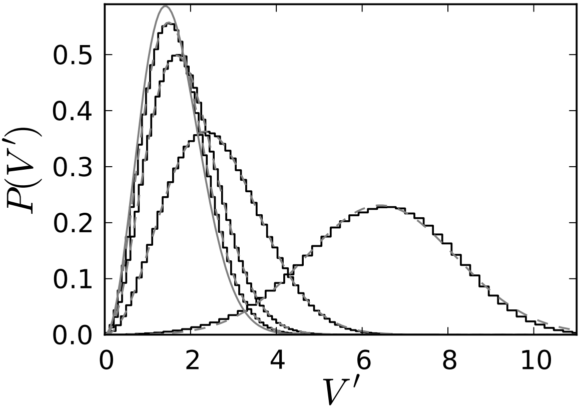


Simulation Results: $\langle V' \rangle$



Simulation Results: $P(V')$

From left to right: $\sigma = 3, 5, 7$ and 9



Predicting the onset of self-propulsion

$$\partial_t n_B(\mathbf{r}, t) = D\nabla^2 n_B(\mathbf{r}, t) - k_2 n_B + \mathcal{S}(\mathbf{r}, t)$$

- D is the diffusion coefficient of the fluid
- k_2 is the bulk rate of the reverse reaction
- $\mathcal{S}$ is the source term on the surface of the colloid that we approximate by a point source
- Balancing against the friction, we obtain a condition for the threshold of the instability:

  $$\mathcal{C} = \frac{4\pi}{3} \frac{k_B T}{\zeta} \frac{R_0^2}{D^2} |\lambda^2| r_f ,$$

  when $\mathcal{C} = 1$. ζ is the friction coefficient, λ is the Derjaguin length and r_f the reaction rate per unit area

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  when $\mathcal{C} = 1$. ζ is the friction coefficient, λ is the Derjaguin length and r_f the reaction rate per unit area
- In the units of the simulations, the critical radius of the particle is $\sigma \approx 4.7$

Outline

Conclusions

- We proposed
  - a model for the self-propelled Janus particle
  - new mesoscopic reactive schemes to explore phoretic mechanisms
- The methodology is very flexible and allows to build machines powered by chemical reactions
- These machines may interact via hydrodynamics and/or chemical concentrations
- We discovered and characterized a mechanism for self-propulsion of symmetric active colloids by symmetry breaking

Perspectives

- Connect the mesoscopic simulations to
  - experimental reality
  - stochastic models
- Use the simulation to discover collective behavior

Bibliography

1. *Phoretic self-propulsion: a mesoscopic description of reaction dynamics that powers motion*
   P. de Buyl and R. Kapral, Nanoscale **5**, 1337-1344 (2013)
   doi:10.1039/C2NR33711H
2. *Self-propulsion through symmetry breaking*
   de Buyl, Mikhailov and Kapral, EPL **103** 60009 (2013)
   doi:10.1209/0295-5075/103/60009
3. de Buyl and Kapral, in preparation (2013): general properties of the $A + C \to B + C$ Janus model

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