Presented at the COMSOL Conference 2009 Milan

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Motility of Catalytic Self-Propelled Nanorods: Modeling with COMSOL Multiphysics

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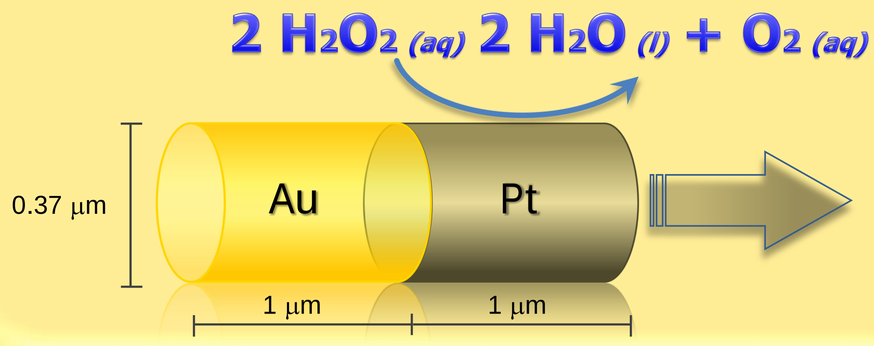
Introduction

A small particle or a nano-sized object placed in a liquid is subject to random collisions with solvent molecules. The resulting erratic movement of the object is known as Brownian motion, which, in Nature, cannot be used to any practical advantage both in natural systems (such as biomolecular motors) or by artificial devices. If energy is supplied by external source or by chemical reactions, Brownian motion can become biased. A macroscopic example of this type of phenomenon is the spontaneous movement of camphor boats surfing on water.
Recently it has been experimentally observed that rod-shaped particles, 370 nm diameter and consisting of 1 mm long Pt and Au segments, move autonomously in aqueous hydrogen peroxide solutions by catalyzing the formation of oxygen at the Pt end.The rods move predominantly along their axis in the counterintuitive direction of Pt end.[1]



Experimental data

In pure water, the movement of Pt/Au nanorods is Brownian in nature and diffusion coefficients obtained by trajectory analysis are similar to those of pure gold nanorods (Table 1).
In aqueous hydrogen peroxide solutions, the motion of Pt/Au is visibly non-Brownian as they move in the direction of their long axis (Figure 1) with the platinum end forward.

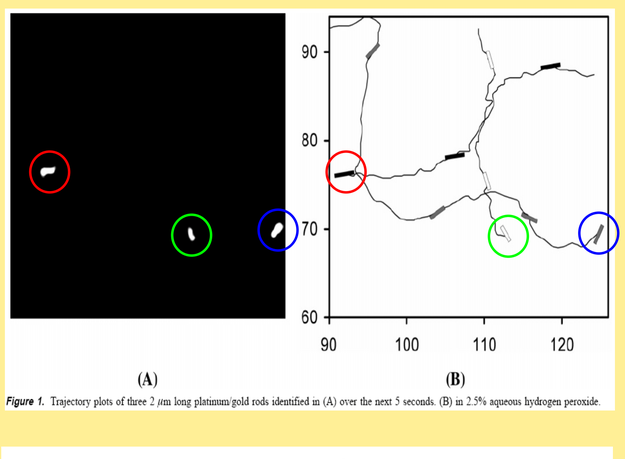


Figure 1. Trajectory plots of three 2 μm long platinum/gold rods identified in (A) over the next 5 seconds. (B) in 2.5% aqueous hydrogen peroxide.

The velocity (Table 2) and directionality (Figure 2) of the nanorods are proportional to the H_2O_2 concentrations.

Table 1. Diffusion Coefficients (in $\mu m^2/s$) for 2 μm Long Platinum/Gold Rods

	sampling interval (seconds)						
experiment	0.1	0.2	0.3	0.4	0.5	1.0	15
Au in H_2O[a]							0.41
Pt/Au in H_2O	0.43	0.41	0.40	0.40	0.39	0.42	
Pt/Au in H_2O_2[b]	4.13	6.61	9.41	11.6	13.8	23.7	

Diffusion coefficients for Pt/Au nanorods in 3.3 % H_2O_2 depend on the duration of the sampling intervals.

Table 2. Effect of Aqueous H_2O_2 Concentration on the Movement of 2 μm Platinum/Gold Rods[a]

H_2O_2 (wt. %)	speed (μm/s)[b]	directionality	v_z (μm/s)[b]
4.9	7.7 ± 0.9	0.78	6.6 ± 1.0
3.3	7.9 ± 0.7	0.75	6.6 ± 0.7
1.6	5.6 ± 0.6	0.65	4.0 ± 0.8
0.33	4.9 ± 0.3	0.60	3.4 ± 0.4
0.031	3.9 ± 0.5	0.19	0.9 ± 0.4
pure water	3.7 ± 0.3	0.07	0.4 ± 0.1

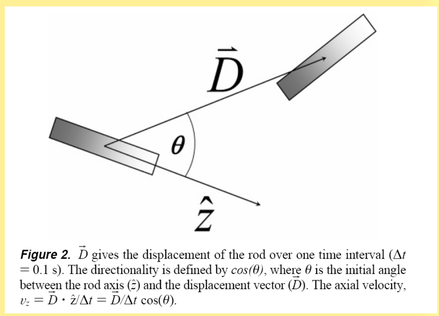


Figure 2. $\vec{D}$ gives the displacement of the rod over one time interval (Δt = 0.1 s). The directionality is defined by $cos(\theta)$, where θ is the initial angle between the rod axis ($\hat{z}$) and the displacement vector ($\vec{D}$). The axial velocity, $v_z = \vec{D} \cdot \hat{z}/\Delta t = \vec{D}/\Delta t \cos(\theta)$.

For 2 μm long Pt/Au rods, the experimentally determinated evolution rate (S) of O_2 from 3.7% H_2O_2 is 9.74×10^{-16} mol/s per rod.
Diffusion coefficient (D) of O_2 is 2.42×10^{-9} m^2/s

Interfacial tension model

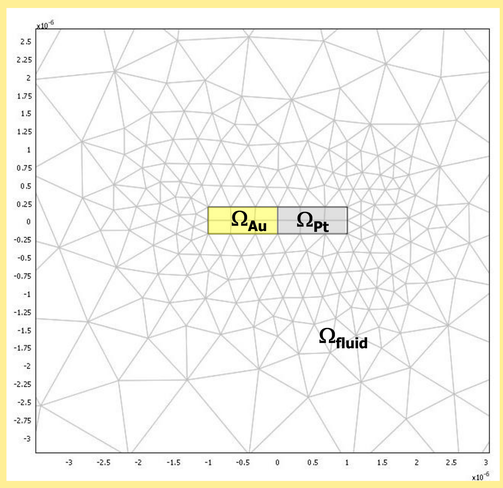
The motion of the rod is toward the region of high concentration of O_2. $\nabla[O_2]$ creates an asymmetric interfacial tension gradient arount Pt/Au nanorod that induces a slip velocity at the rod-fluid interface.[1-3]
Solving the Diffusion-Convection equation for O_2 in the frame of moving rod, one can predict the rod velocity:

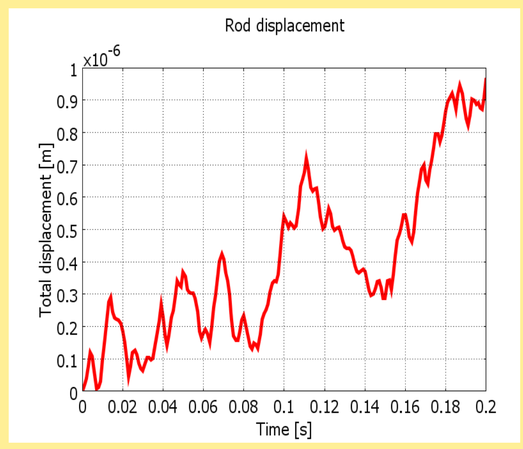
$$v \propto \frac{SR^2\gamma}{\eta DL}$$

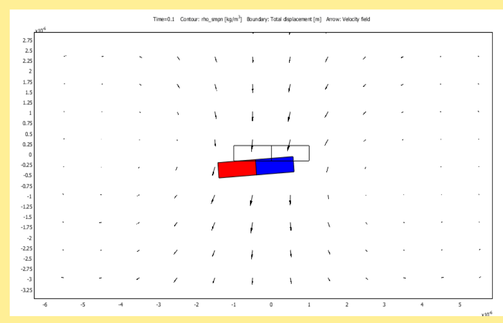
S = surface-normalized O_2 evolution
γ = surface tension of bulk solution
η = liquid viscosity
D = O_2 diffusion coefficient
R = radius of the rod
L = length of the rod

Modeling in Comsol Multiphysics

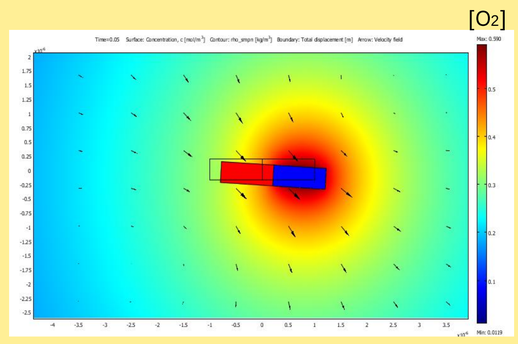
- The Plain Strain application mode solves the model's structural mechanics, and it's active only for the Pt/Au rod domains (Ω_{Au} and Ω_{Pt}).
- The Moving Mesh (ALE) application mode solves for the deformed mesh, moving the boundaries with a moving grid.
- The Incompressible Navier-Stokes application mode computes for fluid dynamics. It's active only in the fluid domain (Ω_{fl}). It imposes a force on the structure's walls resulting from fluid pressure. A Brownian force is also added, modeled as white noise.
- The Diffusion-Convection application mode solves the mass transport equation calculating the concentration of O_2 produced at the catalytic surface in the reference frame co-moving with the rod.







In pure water



In 3.7% H_2O_2

References

[1] W.F. Paxton, K.C. Kistler, C.C. Olmeda, A. Sen, S.K. St.Angelo, Y. Cao, T.E. Mallouk, P.E. Lammert, V.H. Crespi, *J. Am. Chem. Soc.* **2004**, *126*, 13424.
[2] J.R. Howse, R.A.L. Jones, A.J. Ryan, T. Gough, R. Vafabakhsh, R. Golestanian, *Phys. Rev. Lett.* **2007**, *99*, 048102
[3] W.F. Paxton, A. Sen, T.E. Mallouk, *Chem. Eur. J.* **2005**, *11*, 6462.

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