

Project Title: Transport properties of self-propelled micro-swimmers

Name: Dr. Franco Nori (team leader)

Dr. Pulak Kumar Ghosh

Laboratory at RIKEN: Theoretical Quantum Physics Laboratory

I. Background And Purpose:

Artificial microswimmers are active particles capable of autonomous propulsion [1-3]. Their propulsion mechanism, which is often presented as a biomimetic counterpart of cellular motility, is a stationary nonequilibrium process triggered by the particles themselves. Owing to a built-in functional asymmetry, they harvest kinetic energy from their environment; for instance, by inducing local (electric, thermal, or chemical) gradients in the suspension medium (selfphoresis). The simplest class of artificial swimmers investigated in the literature is the so-called Janus particles (JP), mostly spherical colloidal particles with two differently coated hemispheres, or "faces". A different face functionalization determines a peculiar dipolar symmetry, which makes the axial propulsion of these particles possible.

Among the prominent applications of artificial microswimmers is their pharmaceutical usage to control chemical reactions, either as motile catalysts or reactant carriers, in the context of recently proposed smart drug delivery systems. Since self-propelled particles undergo persistent Brownian motion with finite correlation time (also termed active Brownian motion), one expects that the chemical processes they initiate are governed in time and space by their diffusive properties. Indeed, a single molecular reaction takes place only after the involved active agent has diffused close to a reactant molecule, while the reaction itself is assumed to occur instantaneously. We refer to this class of processes as active diffusion limited reactions (DLR).

Diffusion limited reactions in low dimensions and in numerous constrained geometries exhibit anomalous behavior, in the sense that their kinetics is not governed by the classical macroscopic laws of

mass action, but rather by the non-equilibrium dynamics of the reactants.

For instance, in the bimolecular DLR, $A + B \rightarrow 0$, if the initial densities of the A and B reactants are the same, in an infinite volume of Euclidean dimensions $d \leq 4$, these densities decay asymptotically with time like $t^{-\alpha}$, with $\alpha = d/4$ [4,5]. This result is in apparent contrast with the exponent $\alpha = 1$ predicted by the classical rate law. Another paradigmatic DLR that exhibits anomalous kinetics is the bimolecular reaction $A + A \rightarrow 0$, where the reactant density decays with time also according to a power law, but with exponent $\alpha = d/2$.

Keeping mind all recent relevant advances of research in this direction, we investigate the one- and two-dimensional diffusion limited reactions $A + A \rightarrow 0$ and $A + B \rightarrow 0$ with A active Janus particles and B passive particles in thermal equilibrium [6]. We show that by increasing the self-propulsion time of the A particles, the reactant densities decay faster, at least for time transients of potential interest for chemical applications, e.g., to develop smart drug delivery protocols. Asymptotic and transient density decays obey power laws with exponents that depend on the actual annihilation reaction and its dimensionality.

II. Model

We consider a mixtures of n_A A-particles and n_B B-particles with $n_A = n_B$. The mixtures were confined to a segment of length L for $d=1$ and a square of area L^2 for $d = 2$. The active particles considered here are two-dimensional JPs, that is two-faced disks of (small) radius r_0 , corresponding to (low) packing fractions (see Fig1). The free dynamics of a single diffusing particle of unit mass ($m=1$) obeys the Langevin equations,

$$\ddot{x}_i = -\gamma\dot{x}_i + \gamma_0 \cos \phi_i + \gamma\sqrt{2D_0}\xi_i^x(t) \quad (1)$$

$$\ddot{y}_i = -\gamma\dot{y}_i + \gamma_0 \sin \phi_i + \gamma\sqrt{2D_0}\xi_i^y(t) \quad (2)$$

$$\dot{\phi}_i = \sqrt{2D_r}\xi_i^\phi(t). \quad (3)$$

The particle with instantaneous position $\{x_i, y_i\}$ diffuses in the force field under the combined action of self-propulsion and equilibrium thermal fluctuations. $\{\xi_i^x, \xi_i^y\}$ are components of random thermal fluctuation, responsible only for translational diffusion, is modeled by a Gaussian white noises with,

$$\langle \xi_i^q(t) \rangle = 0$$

$$\langle \xi_i^q(t) \xi_j^{q'}(0) \rangle = 2\delta_{ij}\delta_{qq'}\delta(t)$$

Where q or $q' = \{x, y\}$. The thermal noise strength, $D_0 = k_B T / \gamma$ can be estimated by measuring the translational diffusion of a free JP in the bulk in the absence of propulsion. In equations (1-2), γ plays the role of an effective viscous damping constant incorporating all additional effect that are not explicitly accounted for in Eq. (1-2), like hydrodynamic drag, particle-wall interactions, etc.

The propulsion velocity v_i , with modulus v_0 , directed making an angle ϕ_i with respect to the laboratory x -axis. Due to rotational diffusion of the particle, ϕ_i changes randomly, which can be described as a Wiener process, as described in eq.(3), with following statistical properties

$$\langle \xi_\phi(t) \rangle = 0$$

$$\langle \xi_\phi(t) \xi_\phi(0) \rangle = 2\delta_{ij}\delta(t)$$

The rotational diffusion constant D_r is related to the viscosity (η_v) of the medium, temperature (T) and size of the particle. For spherical particle with radius a , rotational diffusion constant can be expressed as $D_r = k_B T / 8\pi\eta_v a^3$. However, rotational diffusion may contain contribution of gradient fluctuations that are very much related to mechanism of acquiring self-propulsion. The mechanisms and origins of the translational and rotational diffusion may not be the

same. Thus, D_0 , v_0 , and D_r can be treated as independent model parameters.

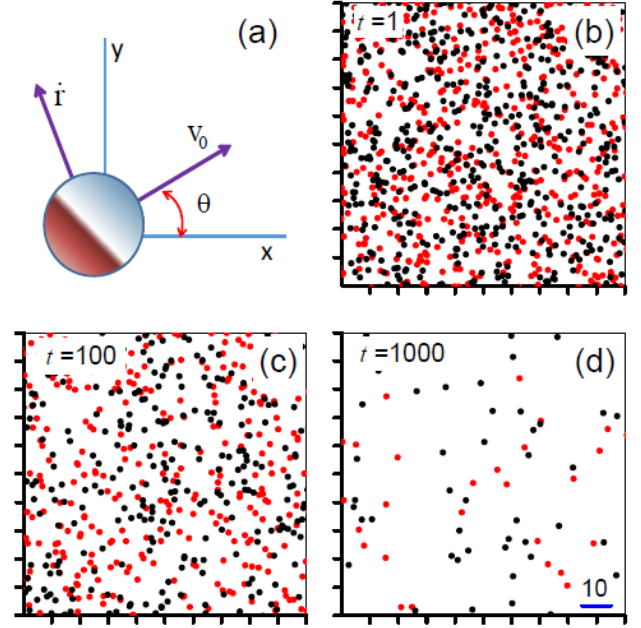


Fig.1: Two dimensional active JP model (see text). The dynamical and the self-propulsion velocities are represented by distinct vectors. (b)-(d) Snapshots of a 2D A-B mixture at three different times in a 100 x 100 sampling region. The simulation box with side $L=1000$ contained $n_A = 5 \times 10^4$ active A particles (JP, red) and $n_B = 5 \times 10^4$ passive B particles (black, circle size not to scale). All particles are disks of radius $r_0 = 0.05$, to ensure a very low initial box packing fraction. Upon collision the A-B pairs annihilate, $A+B \rightarrow 0$, while all other collisions are elastic. Reflecting and periodic conditions at the box boundaries return the same decay law.

III. Numerical simulations method

When simulating a confined particle mixture, one has to specify the collisional processes, as well: (i) Non-annihilating particle collisions were assumed to be elastic. Note that, in 1D, particles of the same species are non-passing and thus tend to form local single files of reduced diffusivity, (ii) collisions against the walls of the container are always elastic; under this condition, walls can be replaced by periodic boundary conditions.

We numerically integrate Eq. (2) by a standard Milstein algorithm to obtain velocity distribution,

diffusivity and effusion rate of the both kinds of species in the binary mixture. Numerical integration has been performed with very short time step, 10^{-4} – 10^{-6} , to ensure numerical stability. To avoid biasing the simulation outcome with unwanted spatial structures, we imposed random initial conditions; that is, uniform spatial distributions, Gaussian velocity distributions with temperature T , and uniform angular distributions of the vector \mathbf{v}_0 for active particles. We examine the inter-particle distances at each step of integration. We assume products are formed as soon as the particles collide each other.

IV. Results and Discussion

Based on the above-mentioned model and simulation scheme we investigate diffusion-controlled reaction of active particles and active-passive mixture. The main results of our numerical investigation can be summarized as follows:

(i) Similarly to inertia reported in [5], the persistent Brownian motion of the active A particles suppresses the retarding effects of spatio-temporal fluctuations in the mixture configuration. Indeed, a general feature of all Fig.2 panels is the fast time decay of $\rho(t)$ for small D_r (large rotational relaxation time). This applies also for large γ where the inertia effects are negligible.

(ii) The faster decays of $\rho(t)$ at low D_r , quantified by the β exponents, are transient effects. Indeed, almost all curves plotted in Fig. 2 hint at approaching the corresponding diffusive decay law, $t^{-\alpha}$ already for t tends to infinity. [Exceptions are mentioned in item (iv).] This is not surprising, because, for $1/\gamma \gg 1/D$, active Brownian motion is indistinguishable from a regular Brownian motion with enhanced diffusivity. At sufficiently low reactant density, that is, for large

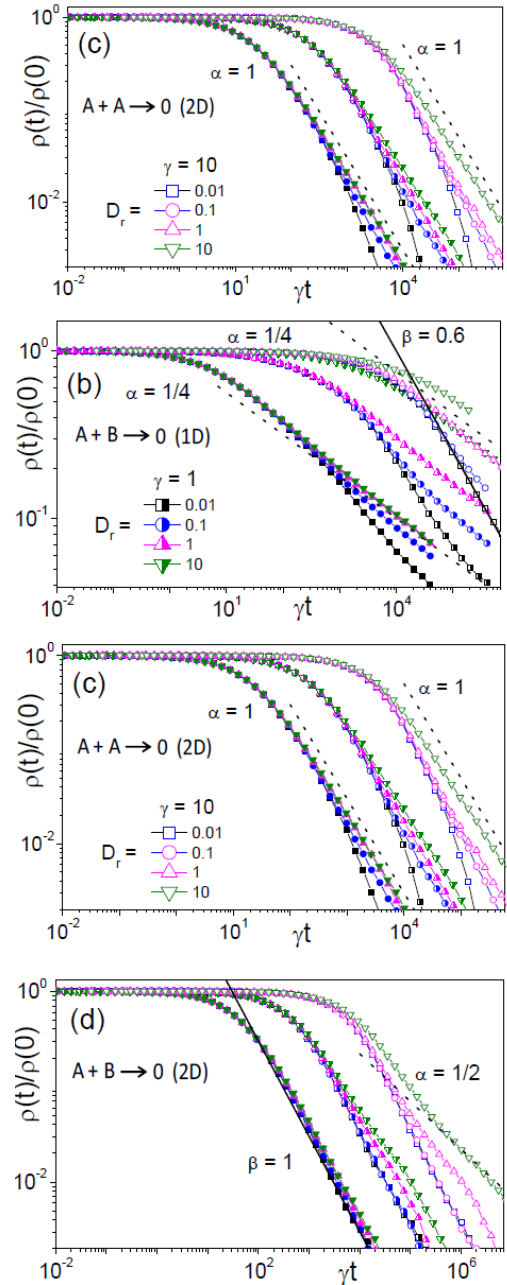


Fig 2: Time decay of the A particle density $\rho(t)=\rho_A(t)$ for: (a), (c) $A+A \rightarrow 0$, (b),(d) $A+B \rightarrow 0$, (a),(b) $d=1$ and (c),(d) $d=2$ and different γ . Here, A are active particles with $v_0 = 1$ and different angular rates, D_r (see legend); B are passive particles. The exponents α and β of the diffusive (large D_r) and transient ballistic (low D_r) time decays are written next to the dashed and solid lines, respectively; α and β do not change by halving or doubling the mixture packing fraction. Simulation parameters: (a) $n_A=3 \cdot 10^4$, $L=10^6$; (b) $n_A = n_B = 5 \cdot 10^4$, $L = 10^3$; (c) $n_A=3 \cdot 10^4$, $L=10^6$; (d) $n_A = n_B = 5 \cdot 10^4$, $L = 10^3$; Other simulation parameters are: $r_0 = 0.05$, $kT=0.2$, $m=1$; all length are expressed in arbitrary units. Legends in (a)-(c) apply to all four panels.

spatial separation of the reactant pairs, the self-propulsion memory of the pair constituents becomes negligible.

(iii) Persistence effects in the self-propulsion mechanism imply that, at high Péclet numbers, the motion of the A particles is ballistic for time interval of the order of $1/D_r$. This reflects in the values of the β exponents of panels (c) and (d).

(iv) Deviations from the general picture of items (ii) and (iii) appear at low γ and D_r , due to the interplay of inertia and persistent activation effects. In that dynamical regime, simulation time was not large enough to assess the asymptotic decay of the mixture density. We notice that, for practical applications, such a regime is of lesser interest as active JPs operate at low Reynolds numbers.

In conclusion, we investigated the role of active diffusive particles in the broad context of the so-called diffusion limited chemical reactions. We restricted our presentation to the archetypal reactions of pair annihilation, $A + A \rightarrow 0$ and $A + B \rightarrow 0$, in one and two dimensions. Moreover we considered the simplest realization of an artificial microswimmer consisting of an active Janus particle. Most of our results are based on simulation data and phenomenological arguments. Despite all the simplifications listed above, we gathered evidence of the capability of artificial micro-swimmers to accelerate the chemical kinetics they assist, either as catalysts or reactant carriers. Such a capability grows prominently in low dimensional or strongly constrained geometries. In particular, we proved that self-propellers have a mixing or stirring effect on the configurational fluctuations occurring in the reactant mixture, which speeds up the annihilation processes.

From a more fundamental point of view, we highlighted the role of memory effects in the diffusive mechanism controlling this class of chemical reactions. Such effects, scarcely addressed in the specialized literature become now experimentally accessible by making use of active

micro- or nanoparticles, since these diffuse with correlation times governed by the same external mechanisms also regulating their motility.

In addition to the research works described above, we are still working on other issues from last year's proposed research, and in particular on entropic and hydrodynamic effects in the dynamics of active Brownian particles diffusing in confined geometries.

V. Future plan

More simulations from last years' proposed research

In the last fiscal year, we have used Hokusai supercomputer mainly to explore diffusion controlled reaction of active particles and hydrodynamics effects in the dynamics of self-propelled particles while diffusing in confined geometries. We have produced some interesting results to capture essential dynamical features of the interacting self-propelled particles in binary mixture. However, the projects on hydrodynamic interaction required some more simulations to be completed.

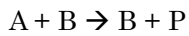
In the fiscal year 2019, in addition to the above item we intend to explore the following issues related to dynamics of active as well as passive particles.

Auto-catalytic reaction by active particle:

One of the most promising applications of Janus particles is catalyzing chemical reactions by interacting with components in reaction mixtures. Catalytic activity is a unique property of Janus particles as well as of other nano-to-micro sized particles. This property is due to presence of a quite large percentage of atoms on the particle's surface with vacant coordination sites. Kinetics of catalytic reactions by passive nano-particles is studied in literature mostly based on macroscopic modeling. However, the details of catalytic activity are dominated by fluctuations statistics in addition to macroscopic laws. Based on a more accurate microscopic picture, we intend to characterize catalytic activity of both self-propelled particles and passive nano-particles. To be specific, we wish to

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explore how self-propulsion of Janus particles can be utilized to enhanced the catalysis rate. To this purpose, the following reaction scheme will be considered,



Here, A is a reactant that converts to the product P, the conversion being assisted by the catalyst B. In our proposal, B might be a passive or active particle with finite recyclability.

Hydrodynamic effects on channels diffusion of rod-like particles: Previous studies on confined diffusion focused mostly on spherical particles. However, microscopic particles with elongated shapes, appear naturally in many situations; examples include colloidal particles, artificial and biological filaments, or DNA strands and micro-swimmers. These earlier investigations suggested that anisotropy makes the diffusive dynamics of a particle significantly more complicated, even in the absence of geometric constraints.

Here, we propose to study how a colloidal rod diffuses in a quasi-two-dimensional corrugated channel. Preliminary simulations reveal that the interplay of channel's spatial modulation and rod's rotational dynamics are likely to causes substantial hydrodynamic and entropic effects. We plan to investigate the separability of these two effects, with the aim of extending the standard Fick-Jacobs theory for spherical particles to incorporate them both. To validate our generalization of this important phenomenological tool, we verified that the resulting theoretical scheme accurately predicts the numerically measured mean first-passage times associated with the rod translational diffusion along the corrugated channel.

Our results will provide the much-needed foundation for the ongoing experimental work [7].

To address the above-mentioned issues we will implement and the numerical scheme mentioned in Sec. III.

Currently, I have a "Quick Use" user account and I would like to get extension of computation facilities for next usage term (up to 31st March 2020) under the same user category.

VI. References

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Usage Report for Fiscal Year 2018

Fiscal Year 2018 List of Publications Resulting from the Use of the supercomputer

[Publication]

[1] Hydrodynamic interaction of trapped active Janus particles in two dimensions

Tanwi Debnath, Yunyun Li, Pulak K. Ghosh, and Fabio Marchesoni, Phys. Rev. E 97, 042602 – Published 9 April 2018

[2] ‘Active Diffusion Limited Reactions’, T. Debnath, P. K. Ghosh, Y. Li, F. Marchesoni, and F. Nori, , JCP (2019) under revision