Chemicaly-Powered Self-Propelled Motors

Raymond Kapral
University of Toronto

G. Rueckner
S. Thakur
P. Colberg
B. Robertson

Y.-G. Tao
P. de Buyl
S.-Y. Reigh

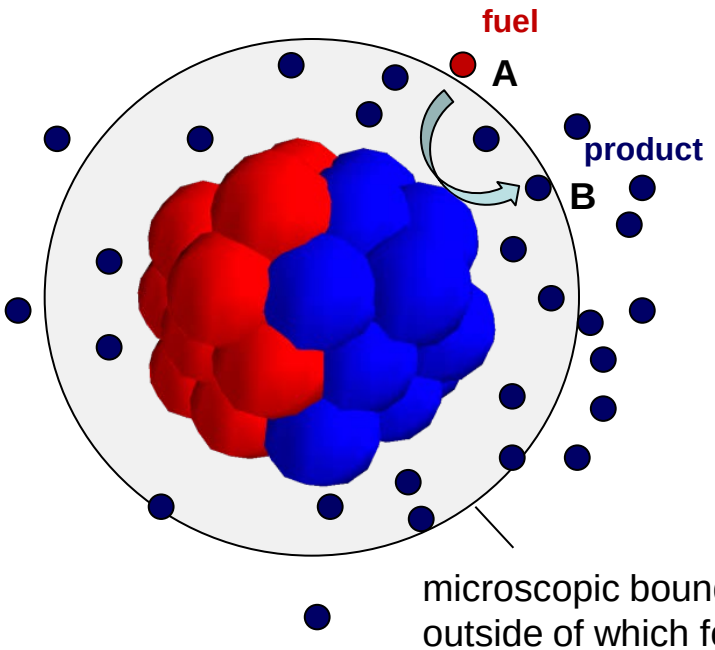
phoretic propulsion of Janus motors

self-diffusiophoresis

-- due to the self-generated concentration gradient from the A → B reaction, the Janus particle experiences an unequal force over its surface within the boundary layer due to intermolecular forces

-- A and B interact differently with the N spheres

-- momentum conservation leads to fluid flow



microscopic boundary layer outside of which forces on Janus particle plus fluid vanish

review, see
RK, J. Chem. Phys. 138, 020901 (2013)

$$V_u = \frac{k_B T}{\eta} \frac{n_0}{3R_m} (\lambda_C^2 + \lambda_N^2) c_1$$

$$\lambda_S^2 = \int_0^\infty dz \; z(e^{-\beta W_{BS}(z)} - e^{-\beta W_{AS}(z)})$$

gauges forces

→ next: two examples where A and B have identical interactions the Janus particle

simulation of self-propelled motion

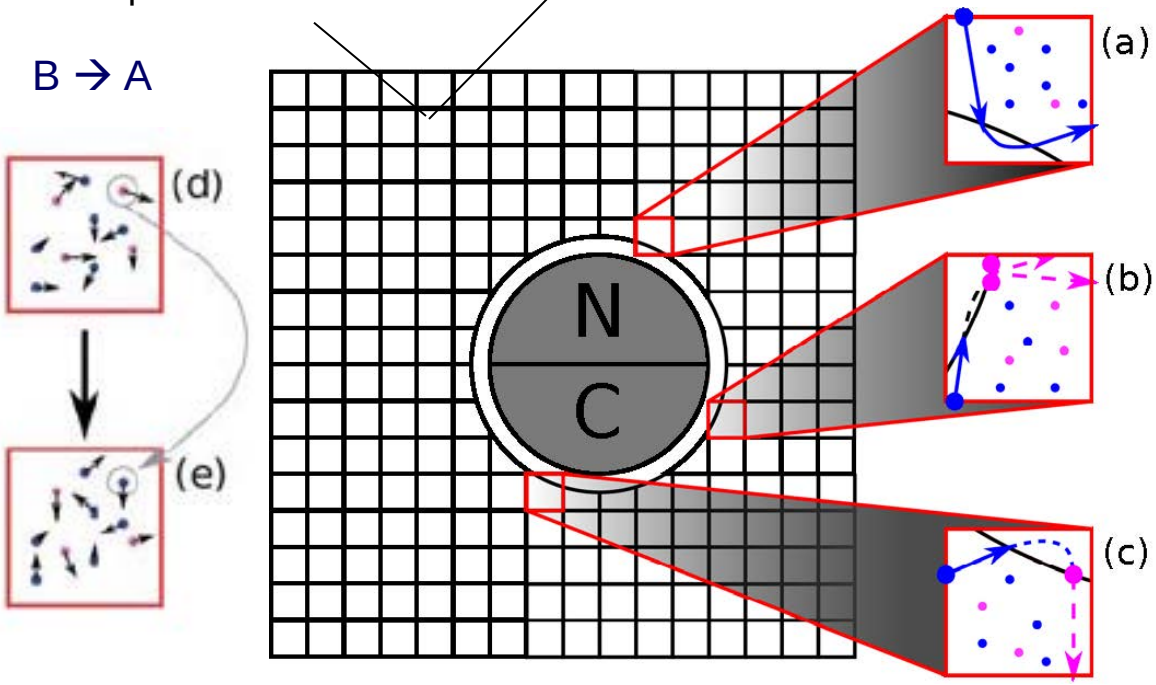
solvent particles interact with motor through intermolecular forces and evolution through MD; solvent evolves by reactive MPCD

bulk reaction B → A to maintain system in a nonequilibrium state

$$\mathbf{v}_i' = \mathbf{V}_\xi + \hat{\omega}_\xi(\mathbf{v}_i - \mathbf{V}_\xi)$$

nonreactive collisions on noncatalytic side

B → A



A → 2B

reactive collisions on catalytic side

A → B $(\pm\Delta u)$

bulk reaction: $\sum_\alpha \nu_\alpha^j X_\alpha \xrightarrow{k_j} \sum_\alpha \bar{\nu}_\alpha^j X_\alpha$

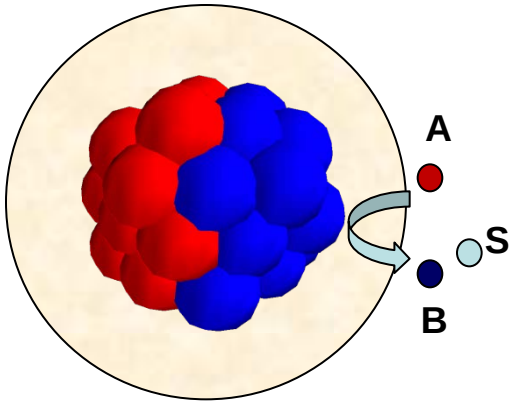
probability: $p_j^\xi(\mathbf{N}^\xi) = \frac{a_j^\xi}{a_0^\xi}\left(1 - e^{-a_0^\xi \tau}\right)$ $\qquad a_j^\xi = k_j(V_c)\prod_\alpha \frac{N_\alpha^\xi!}{(N_\alpha^\xi - \nu_\alpha^j)!}$

- *ex: propulsion by thermophoresis induced by reaction*

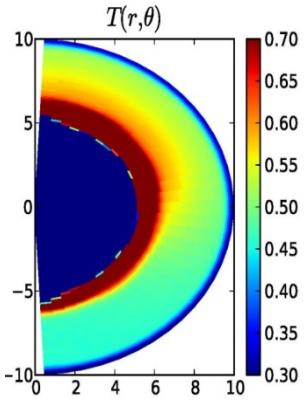
reactive A and B species carry internal energy labels u_A and u_B

on collision with catalytic sites the exothermic reaction $A \rightarrow B + \Delta u,\ \Delta u = u_B - u_A$ occurs induces an Inhomogeneous temperature field

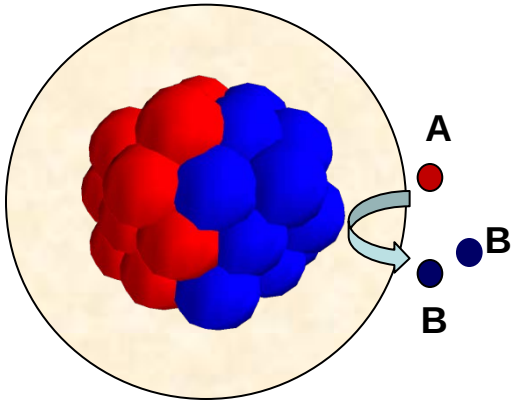
construct reactive collision dynamics to satisfy mass, momentum and energy conservation laws

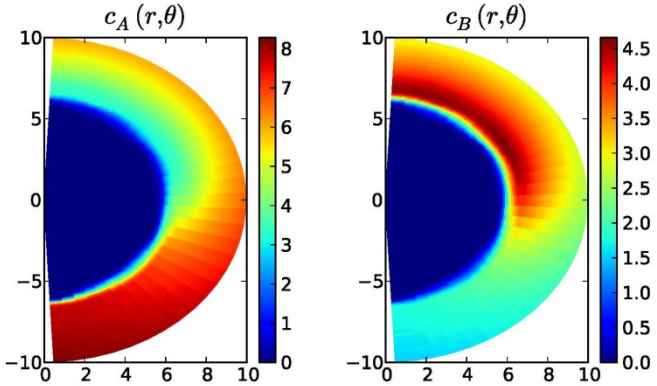


Δu	$\langle V_z \rangle \times 10^3$
0.1	1.5
0.2	2.8
0.3	3.8
0.5	5.7



- *ex: propulsion by dissociation reactions*

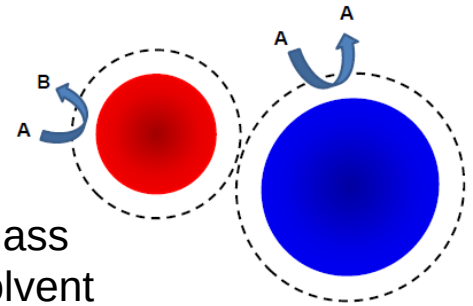




$$\langle V_z \rangle \sim 0.5 \times 10^{-3}$$

de Buyl and RK, Nanoscale, 5, 1337 (2013)

sphere dimers

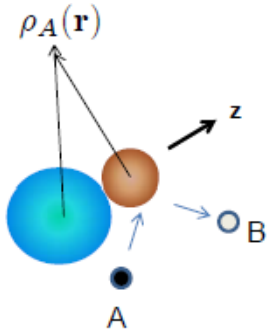


catalytic activity is confined to one of the spheres comprising the dimer

nonequilibrium average force on the dimer center of mass along the dimer in terms of the force exerted on the solvent

$$F_{\rm p} = \sum_{\alpha=A}^{B} \int d\mathbf{r}\ \rho_\alpha(\mathbf{r})\ (\hat{\mathbf{z}}\cdot\hat{\mathbf{r}})\frac{dV_{C\alpha}(r)}{dr}$$

$$+\sum_{\alpha=A}^{B} \int d\mathbf{r}'\ \rho_\alpha(\mathbf{r}'+R\hat{\mathbf{z}})\ (\hat{\mathbf{z}}\cdot\hat{\mathbf{r}}')\frac{dV_{N\alpha}(\mathbf{r}')}{dr'}$$



nonequilibrium average of the microscopic density fields

$$\rho_\alpha(\mathbf{r}) = \langle \rho_\alpha(\mathbf{r};\mathbf{r}^{N_\alpha})\rangle \qquad \rho_\alpha(\mathbf{r};\mathbf{r}^{N_\alpha}) = \sum_{i=1}^{N_\alpha}\delta(\mathbf{r}_{i\alpha}-\mathbf{r})$$

find by solution of RD equation with appropriate BC

for solution of RD equation, see: Popescu, Tasinkevych and Dietrich, EPL, 95, 28004 (2011)

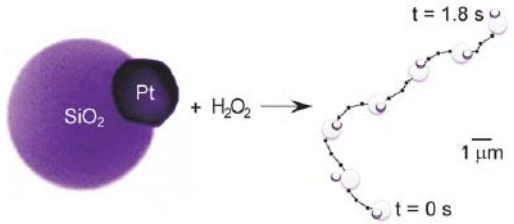
approximation for average propulsion force

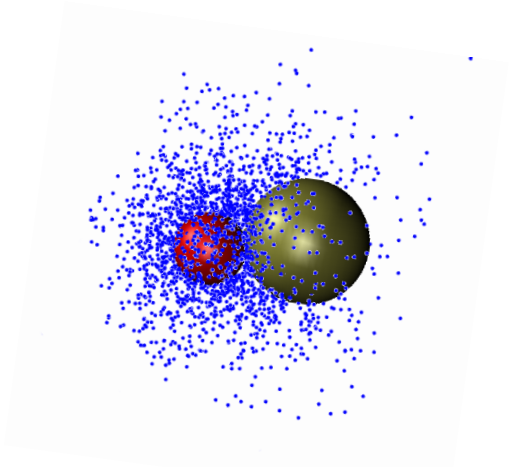
$$F_{\rm p} = -\frac{8\pi}{3} r_f k_B T \frac{R_0^2 R_0^N}{D R^2}\lambda^2$$

reaction rate per unit area

$$r_f = \frac{1}{4\pi R_0^2}\frac{dN_B}{dt} = \frac{k_1^0 k_D}{k_1^0 + k_{-1}^0 + k_D}\frac{n_0}{4\pi R_0^2}$$

sphere dimer dynamics



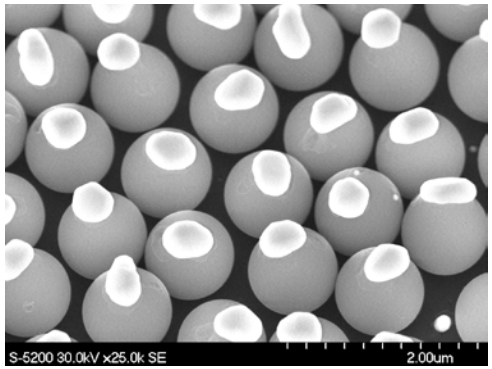


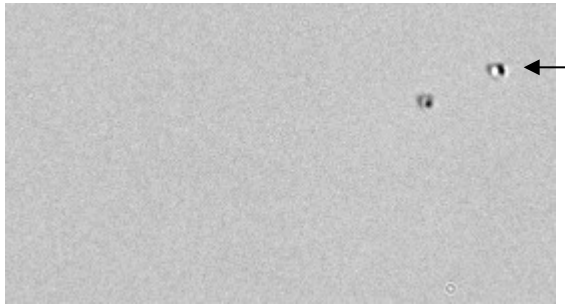
experiments:

Valadares, Tao, Zacharia, Kitaev, Galembeck, RK and Ozin, Small, 6, 565 (2010).

simulations using MD-MPC dynamics:

Rueckner and RK, PRL, 98, 150603 (2007); Tao and RK, JCP, 128, 164518 (2008)





2.4 Hz

8.3 μm/s

$d_N = 8.0$

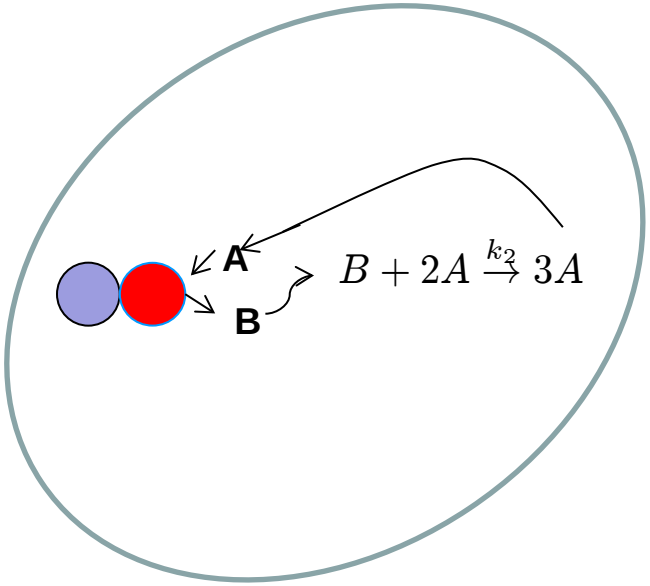
$d_C = 2.0$

$d_C = 4.0$

$d_C = 6.0$

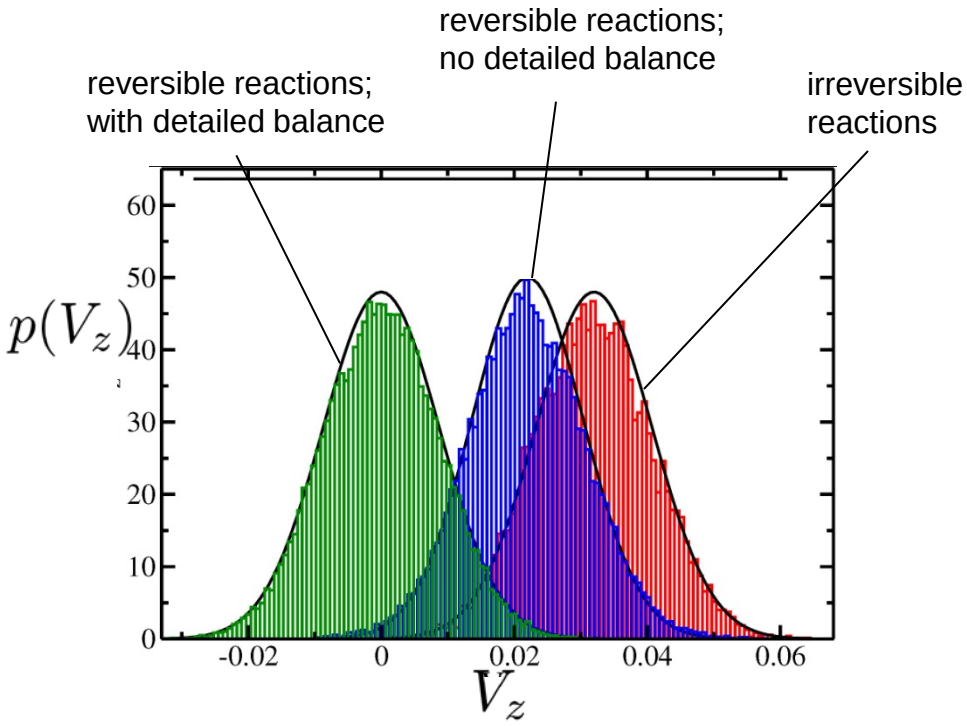
$d_C = 8.0$

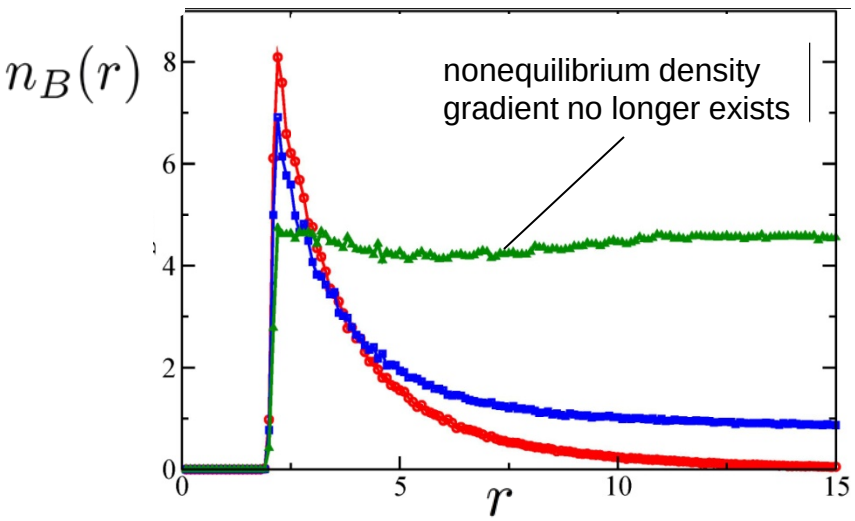
sphere dimer dynamics in active media



an example of dimer propulsion under nonequilibrium conditions

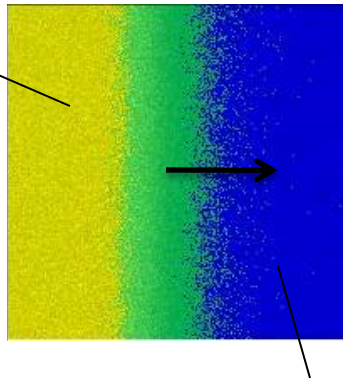
note: product B is consumed in the environment and regenerates the fuel A for the sphere dimer propulsion





Thakur and RK, JCP 135, 024509 (2011)

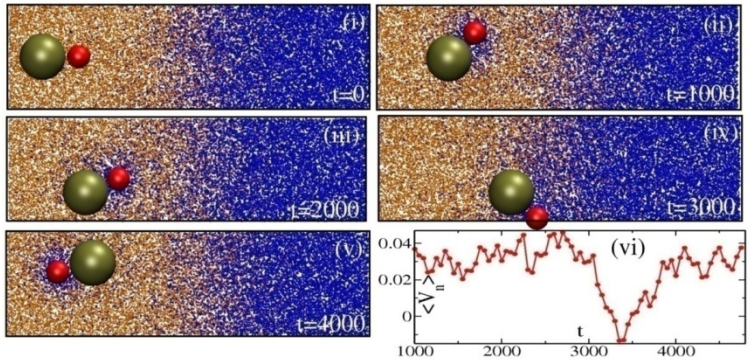
interaction with a chemical wave



bulk phase cubic autocatalytic reaction supports a chemical wave

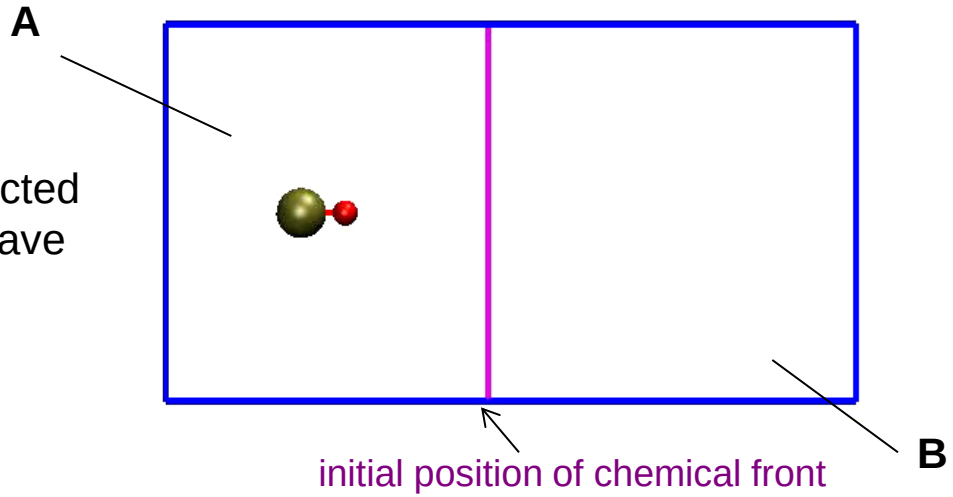
$$B + 2A \xrightarrow{k_2} 3A$$

autocatalyst A consumes B to yield a front that propagates with constant velocity



$$n_B(u) = n_0\left(1 + e^{-cu/D}\right)^{-1}$$

$$c = (k_2 n_0^2 D/2)^{1/2} \qquad u = x - ct$$



nanomotor is reflected by the chemical wave

Thakur, Chen and RK, Angew. Chem. Int. Ed., 50, 10165 (2011)

mean square displacement and motor diffusion

the motor experiences orientational Brownian motion that causes it to tumble and leads to diffusion on long time scales

characteristic orientational relaxation time: $\tau_r = 4\pi\eta R_m^3/k_B T$

mean square displacement

$$\Delta L(t)^2 \approx 6(D_0 + \tfrac{1}{3}V_u^2\tau_r)t - 2V_u^2\tau_r^2\left(1 - e^{-t/\tau_r}\right)$$

ballistic behavior for short times

$$\Delta L(t)^2 \approx V_u^2 t^2$$

linear behavior for times $t \gg \tau_r$

$$\Delta L(t)^2 \approx 6(D_0 + \tfrac{1}{3}V_u^2\tau_r)t$$

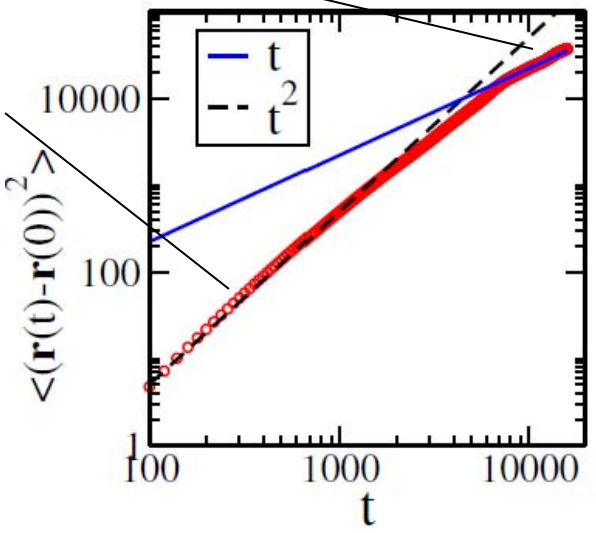
D_0: diffusion coefficient in absence of propulsion

motor diffusion coefficient $D_m = D_0 + \tfrac{1}{3}V_u^2\tau_r$

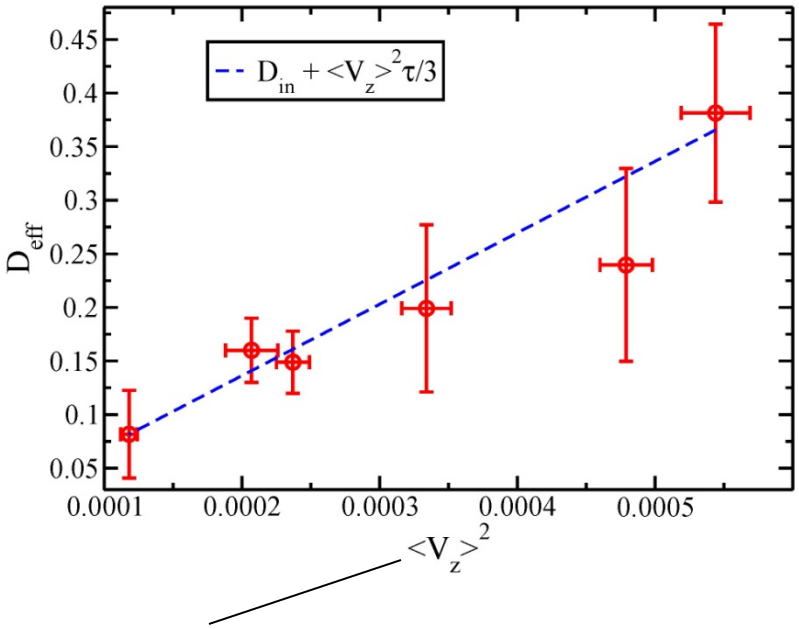
sphere dimer diffusion in an active medium

diffusive regime $\sim t$

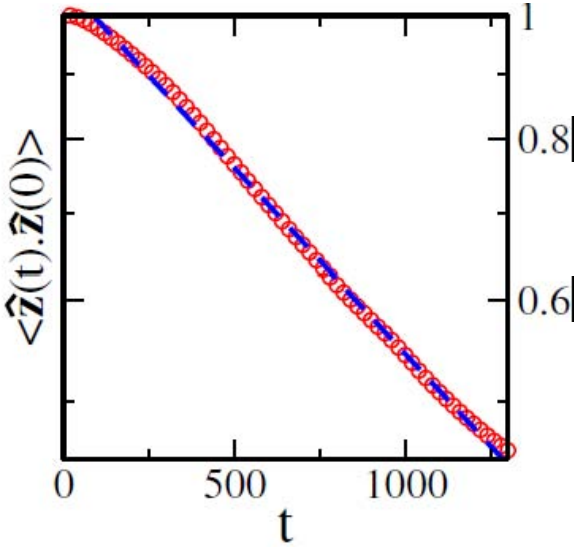
ballistic regime $\sim t^2$



$$D_{\text{eff}} = D_0 + \tfrac{1}{3}\langle V_z \rangle^2 \tau_R$$



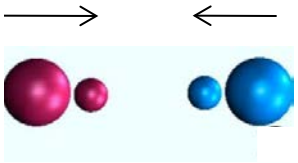
controlled by varying reaction rate in bulk medium



$\tau_R \approx 2000$

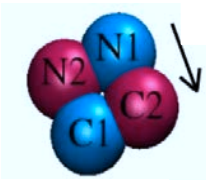
sphere dimers and their interactions

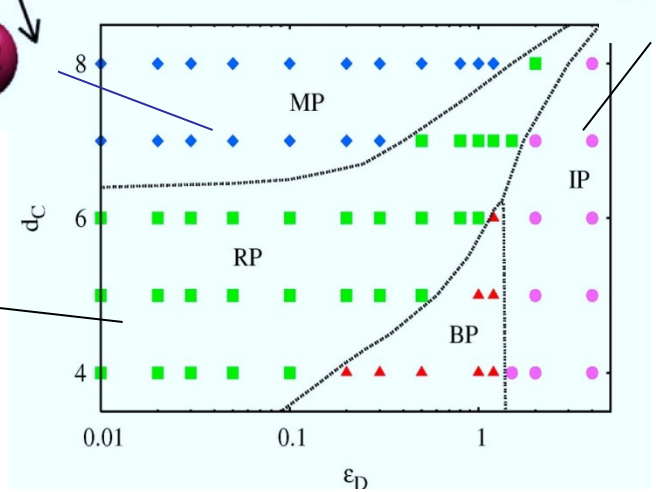
collisions can lead to scattering of dimers or bound pairs; dynamics influenced by chemical gradients, hydrodynamic interactions, direct forces



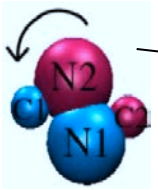
Brownian Pairs

Moving Pairs

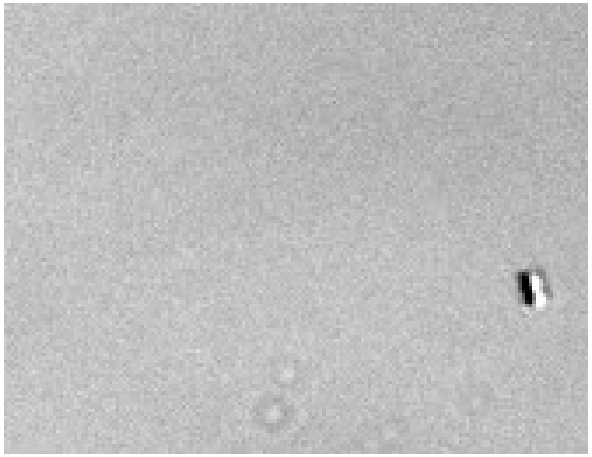




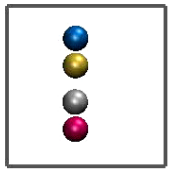
Rotating Pairs



moving bound pairs in sphere dimer experiments

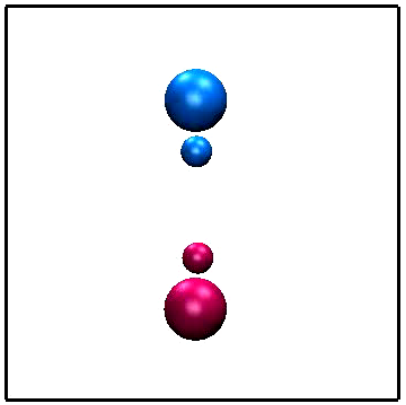


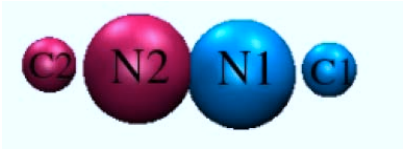
Valadares, Tao, Zacharia, Kitaev, Galembeck, RK and Ozin, Small, 6, 565 (2010).

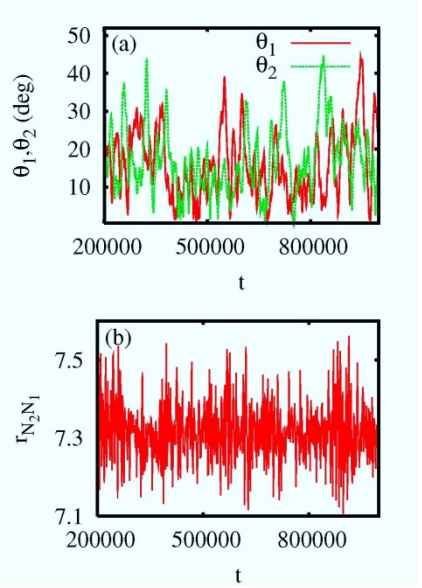


Thakur and RK, J. Chem. Phys., 133, 204505 (2010)

Brownian Pair NN internuclear separation



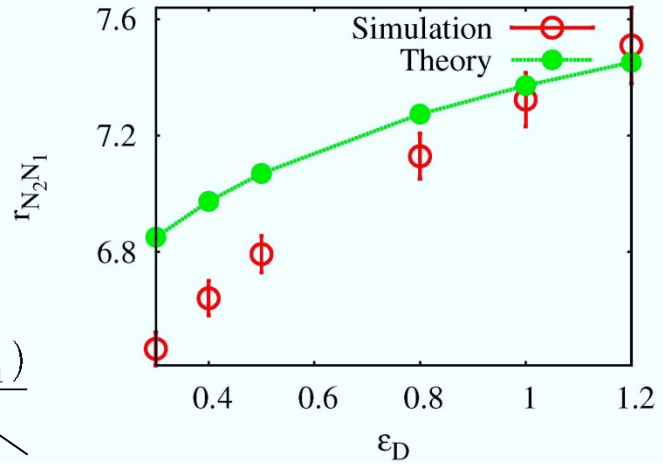




BP is nearly linear and has zero propulsion velocity; can be used to determine the NN internuclear separation

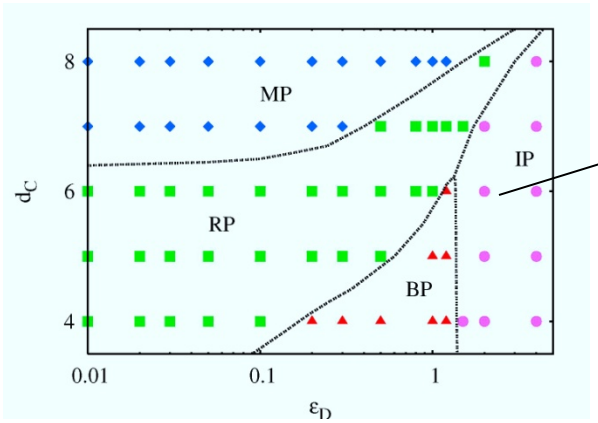
$$0 = \langle \hat{\mathbf{z}} \cdot \mathbf{F} \rangle = \sum_{\alpha=A}^{B} \frac{M_2}{M} \int d\mathbf{r} \rho_\alpha(\mathbf{r}) \frac{\partial V_{\alpha N_1}(r)}{\partial r} (-\hat{\mathbf{z}} \cdot \hat{\mathbf{r}})$$

$$+ \sum_{\alpha=A}^{B} \frac{M_1}{M} \int d\mathbf{r} \rho_\alpha(\mathbf{r}) \frac{\partial V_{\alpha N_2}(r)}{\partial r} (\hat{\mathbf{z}} \cdot \hat{\mathbf{r}}) - (\hat{\mathbf{z}} \cdot \hat{\mathbf{r}}_{N_2 N_1}) \frac{\partial V_{N_1 N_2}(r_{N_2 N_1})}{\partial r_{N_2 N_1}}$$



new interaction term

collective dynamics of many sphere dimer motors

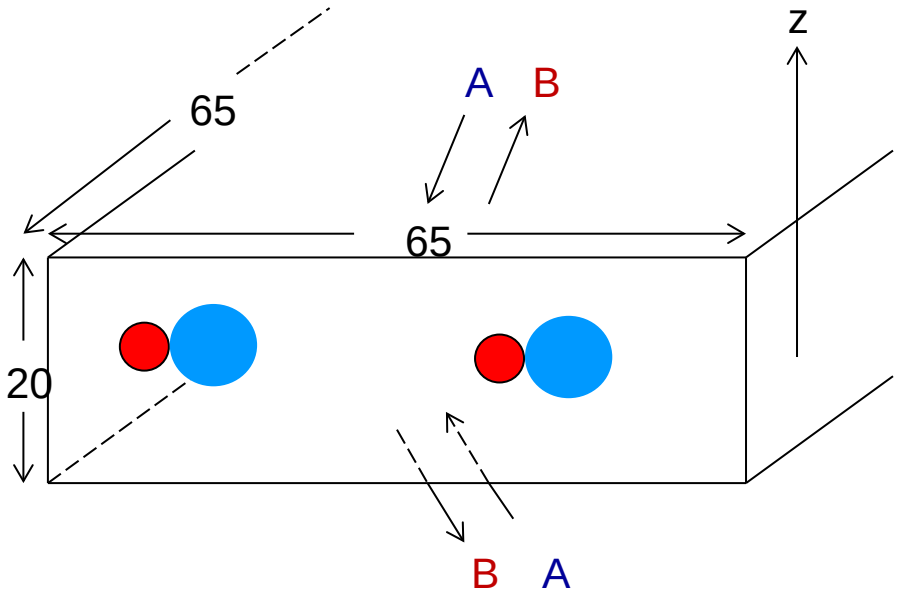


IP region of phase diagram where collisions between isolated dimers do not lead to bound dimer pairs -- increase monomer-monomer repulsion so that long-lived pairs do not form

simulations in slab geometry: fluxes of A and B species at walls perpendicular to z axis to maintain the system far from equilibrium and supply fuel to motors

monomers interact with walls to roughly confine the dimers to the midplane between the walls

solvent experiences bounce-back collisions with walls

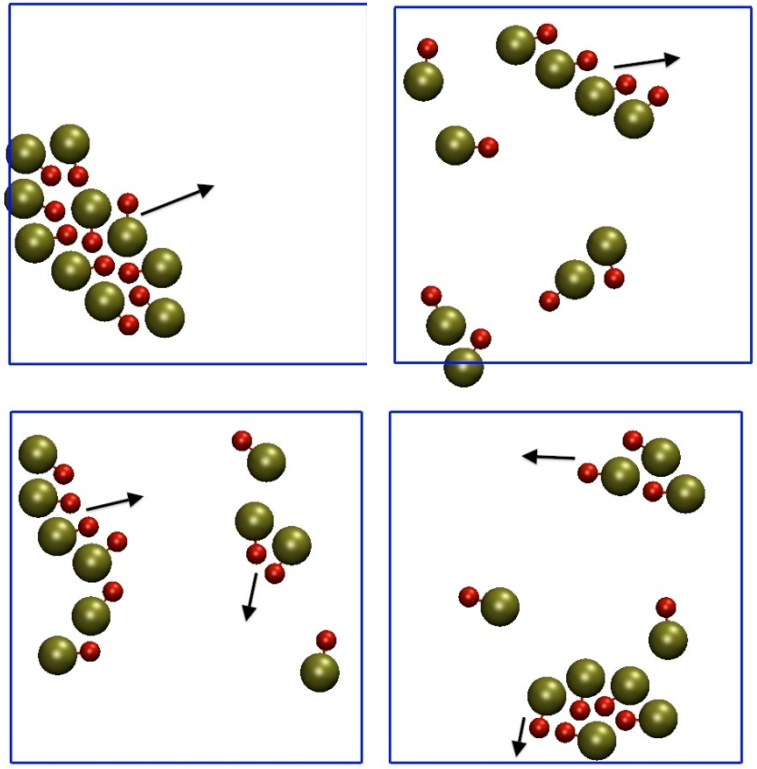


periodic boundary conditions along x and y

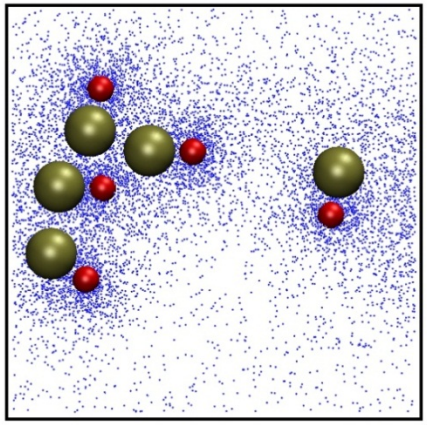
S. Thakur and RK, Phys. Rev. E, 85, 026121 (2012)

active self-assembly

repulsive interactions between monomers on different dimers is so that sphere dimers strongly repel and cannot approach closely for depletion forces to play a role



long-range concentration fields produced by motors influence collective motion



a motor responds to its local concentration gradient and that of its neighbors

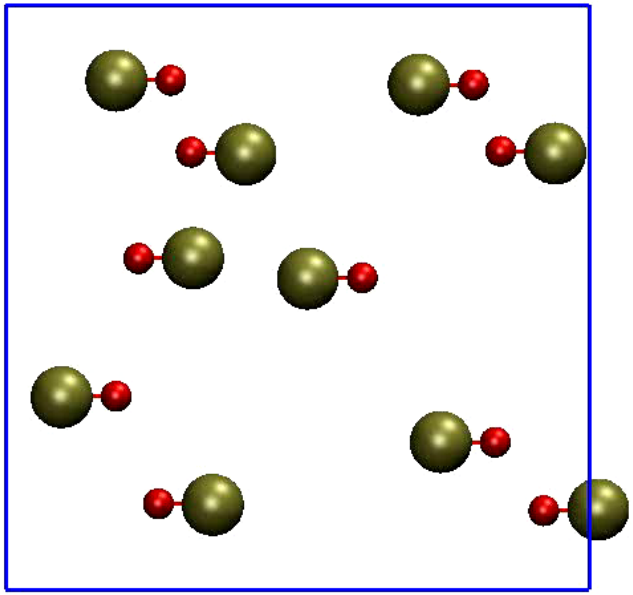
dimer motors move up the gradient and are propelled towards neighboring motors.

when two or more motors approach, they align, since a motor with its N end towards the C end of a neighboring motor will result in a small concentration gradient across the N monomer.

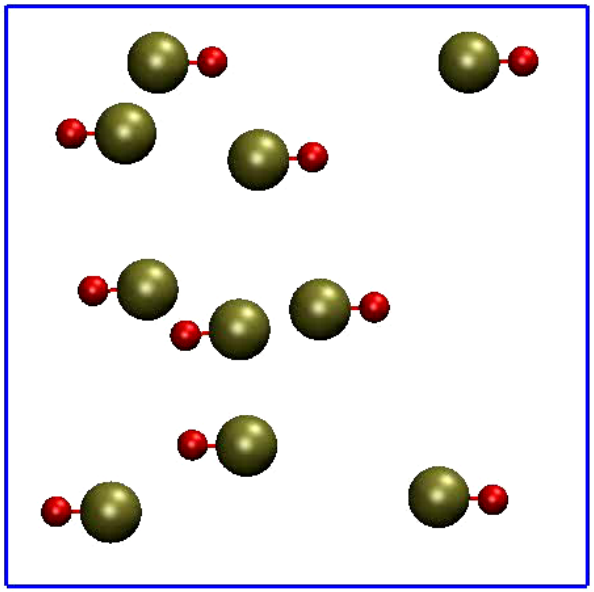
configurations with the majority of motors aligned in a given direction will be self-propelled in that direction, until the aggregate fragments.

self-generated gradients control dynamics

comparison of dynamics with and without chemical reaction



transient swarms of sphere dimers form and move collectively as units for substantial time periods -- in spite of repulsive direct interactions



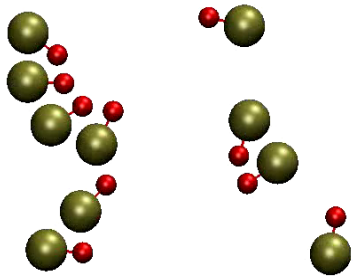
dynamics of dimers without chemical reactions and self-propulsion – no self-assembly takes place

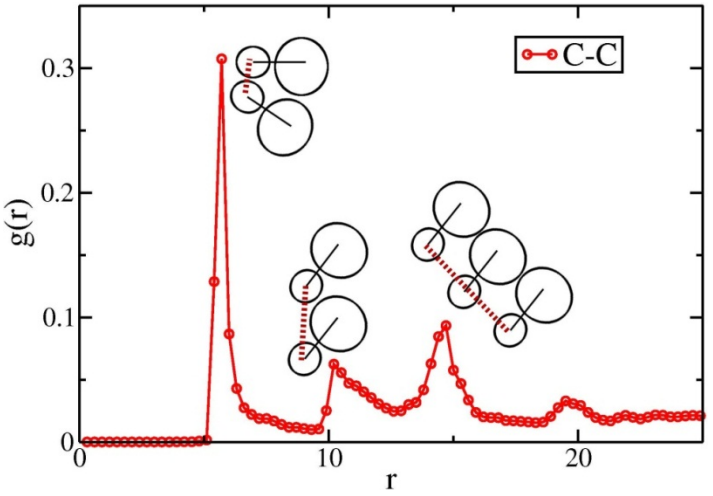
note: self-assembly occurs when hydrodynamic interactions are absent

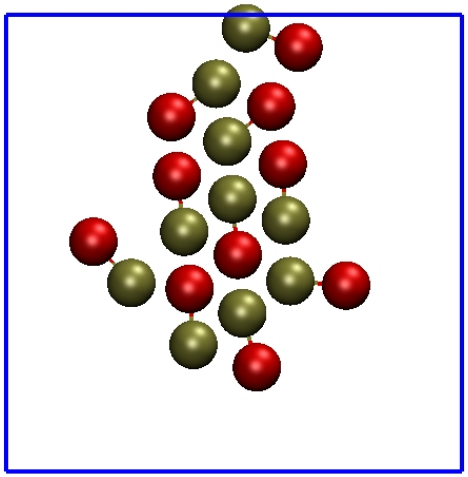
nonequilibrium radial distribution functions

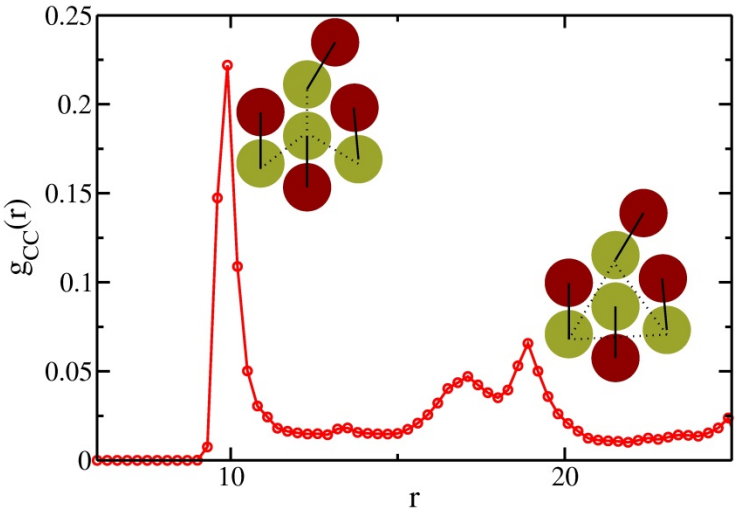
the prevalence of self-assembled sphere dimer swarms gives rise to characteristic spatial correlations which are reflected in the structure of the nonequilibrium radial distribution function

shape matters

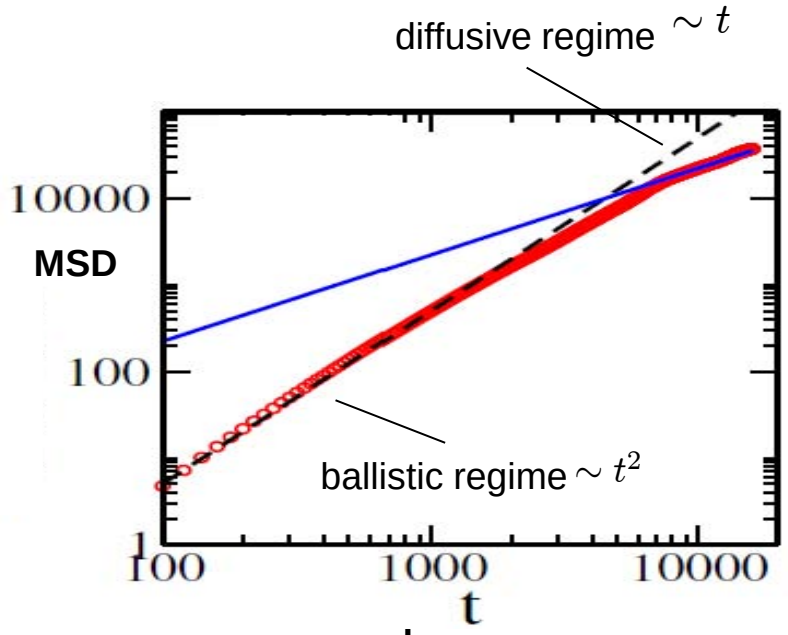




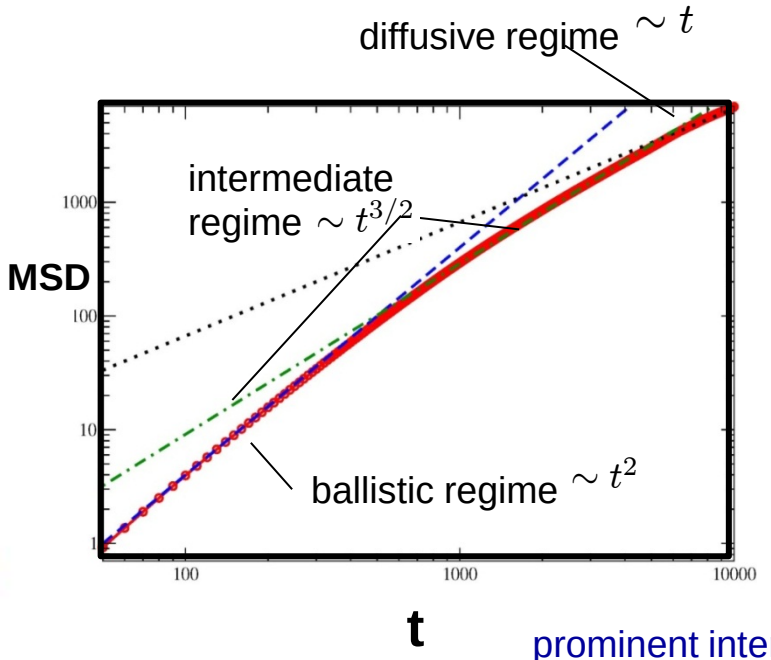




mean square displacement for multi-motor systems



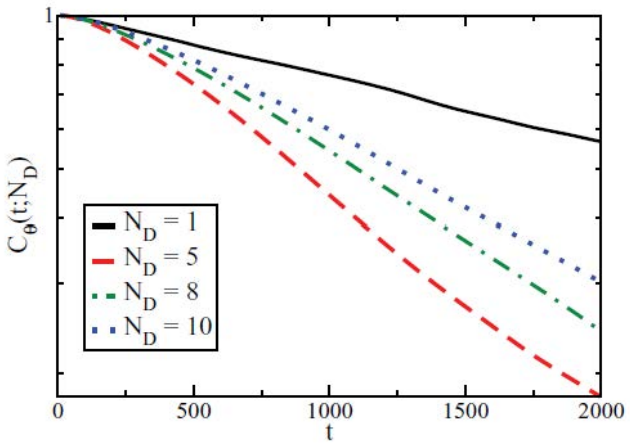
single sphere dimer



10-dimer system

prominent intermediate scaling regime

orientational relaxation



$$C_\theta(t; N_D) = N_D^{-1} \sum_{\nu=1}^{N_D} \langle \hat{\mathbf{z}}_\nu(t) \cdot \hat{\mathbf{z}}_\nu(0) \rangle$$

nonmonotonic behavior with dimer number

$$\tau_R(1) > \tau_R(10) > \tau_R(5)$$

-- dimer-dimer collisions lead to reorientation times shorter than those due to Brownian motion of single dimer

-- for large N locked cluster configurations exist, leading to an increase in the reorientation time

why artificial self-propelled nano-objects deserve our attention

molecular motors are ubiquitous in biological systems and are essential for many important biological functions -- the biological cell is now viewed as a factory where many molecular machines cooperate to carry out biological functions

can we learn how to use artificial motors in a similar way?

-- artificial nanomotors will likely play an increasingly important role when we learn how to use them

– will they change the way we think about the dynamics in complex systems?

basic science -- they are small machines that operate in the far-from-equilibrium and experience strong fluctuations during their operation -- present many challenges for statistical mechanics