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Anomalous Diffusion of Symmetric and Asymmetric Active Colloids

Ramin Golestanian

Department of Physics and Astronomy, University of Sheffield, Sheffield S3 7RH, UK

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The stochastic dynamics of colloid particles with surface activity—in the form of catalytic re-
action or particle release—and self-phoretic effects is studied analytically. Three different time
scales corresponding to inertial effects, solute redistribution, and rotational diffusion are identified
and shown to lead to a plethora of different regimes involving inertial, propulsive, anomalous, and
diffusive behaviors. For symmetric active colloids, a regime is found where the mean-squared dis-
placement has a super-diffusive $t^{3/2}$ behavior. At the longest time scales, an effective diffusion
coefficient is found which has a non-monotonic dependence on the size of the colloid.

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The development of biomimetic technology would sign-
ificantly benefit from the ability to make synthetic com-
ponents with desired motility properties. In recent years,
there has been a range of developments along these lines,
with functionalities that can be manipulated at length
scales ranging from microns down to molecular scales

$\nu$. These include experimental realization of actuated
microswimmers $\nu$ and theoretical proposals of simple
model swimmers that can tackle the problems caused
by low Reynolds number conditions $\nu$. Moreover, it
has been recently demonstrated (both experimentally
and theoretically) that interfacial phoretic effects (such
as electrophoresis, electroosmosis, and diffusiophoresis)
could lead to self-propulsion of colloidal particles $\nu$, $\nu$, $\nu$. It has also been shown that phoretic effects can be used to
steer both active and passive colloid particle $\nu$, $\nu$, which adds to the promise of these phenomena for de-
signing functional self-motile vessels in the nanoscale.

A fundamental property of such small objects, even
when equipped with a self-propulsion mechanism, is that
their motion is stochastic due to the ambient fluctuations
that could be of thermal origin or otherwise. This
means that we cannot directly control the motion of self-
motile objects, and any design characteristic needs to be
incorporated into statistical average outcomes. For ex-
ample, it has been shown that a self-propelled colloidal
particle makes a crossover between ballistic and diffusive
behaviors over a time scale that is set by the rotational
diffusion of the colloid, when its orientation will be ran-
domized $\nu$. A study of a two dimensional model of self-
propelled objects with fluctuations both in direction and
magnitude of the velocity has shown the possibility of re-
entrant ballistic and diffusive behaviors $\nu$. Other ex-
amples include the effect of the activity of proteins on
the dynamics of membranes $\nu$, and collective behav-
ior of mixtures of motors and filaments (or reorganizing
living cells) and active particles such as swimming bacte-
rnia $\nu$, $\nu$, where a host of qualitative and quantitative
changes have been found to occur due to nonequilibrium
fluctuations. In light of this inherent feature, it will be
natural to ask how many distinct regimes of motion we
could have for active colloidal particles, what the relevant
time scales that differentiate between these regimes are,
and how they can be tuned so that the desired type of
motion could be achieved by choosing the right param-
ters.

Here, we aim to address some of these questions for a
class of isolated self-motile active colloids. We study the
velocity autocorrelation function and the mean-squared
displacement of surface-active spherical colloidal parti-
cles that interact with their self-generated surrounding
clouds of solute particles via interfacial phoretic effects.
We identify the relevant time scales in the dynamics,
namely the hydrodynamic relaxation time $\tau_h$ that con-
trols the crossover between inertial and viscous regimes,
the diffusion time of the solute particles around the col-
loid $\tau_d$, and the rotational diffusion time of the colloid $\tau_r$.
We calculate the contribution due to hydrodynamic fluct-
uations, as well as the self-phoretic contributions that
depend on whether the particles are symmetric (in which
case there is no net propulsion) or asymmetric (where the
colloids are self-propelled). We find that these different
contributions lead to a variety of different regimes, as
summarized in Fig. $\nu$. For symmetric surface activity,
we find a regime corresponding to $\tau_h \ll t \ll \tau_d$ where
the active colloid demonstrates a super-diffusive behav-
ior with a mean-squared displacement $\sim t^{3/2}$ (shaded
region in Fig. $\nu$). This is similar and somewhat related

![FIG. 1: Summary of results for the different contributions to the mean-squared displacement of active colloids. The total mean-squared displacement is obtained by summing all of the contributions for asymmetric colloids, and the bottom two rows (only) for symmetric colloids.](image-url)
to an anomalous super-diffusive regime found in active bacterial suspensions \[12\]. Other regimes include inertial \(t^2\) or propulsive \(t^\beta\) behaviors, diffusive behavior \(\sim t\), and an anomalous correction of the form \(-\gamma t^{3/2}\).

We consider a spherical colloidal particle of radius \(R\) with an axially symmetric pattern of surface activity as shown in Fig. 2a, which in essence leads to the release of (excess) product particles \(P\) with diffusion coefficient \(D\). This could correspond to a chemical reaction \(S \rightarrow S' + P\) catalyzed on the surface of the colloid, with the simplifying assumption that one of the product particles is very similar to the substrate, or a container that releases particles through channels.

The stochastic nature of the colloid causes the cloud of product particles to constantly redistribute, which will in turn make the velocity of the active colloid fluctuate. To get the instantaneous velocity of the colloid, we need to solve the diffusion equation for the concentration profile of the product particles, namely

\[
\partial_t C(r, t) - D \nabla^2 C(r, t) = \alpha(\theta, \phi, t) \delta(r - R),
\]

subject to the boundary condition of vanishing normal current on the surface of the sphere. In Eq. (1), \(\alpha(\theta, \phi, t)\) is the surface activity function of the sphere, \(i.e., rate per unit area of the introduction of (excess) product particles.

For axially symmetric surface activity, we can represent the function in terms of the spherical harmonics as

\[
\alpha(\theta, \phi, t) = \sum_{\ell, m} \left( \frac{4\pi}{(2\ell + 1)} \right) \alpha_{\ell, m}(\theta_n(t), \phi_n(t)) Y_{\ell m}(\theta, \phi).
\]

Equation (1) only gives the average density, and the linear relation between the velocity and the concentration profile suggests that in order to calculate velocity correlations we need to incorporate the density fluctuations as well, which we do using the method outlined in Ref. \[6\].

Using the formulation described above we can calculate the velocity autocorrelation function for the active colloid \(A_{\text{sym}}(t) \equiv \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle\) as well as the mean-squared displacement \(\Delta L^2(t) \equiv \langle (\mathbf{r}(t) - \mathbf{r}(0))^2 \rangle\). There are three important time scales in the problem. The characteristic diffusion time of the product particles around the sphere is \(\tau_d = R^2/D\), where \(D = k_B T/(6\pi \eta a)\) depends on the radius of the solute particles \(a\). This time scale sets the relaxation time of the redistribution of the particles around the sphere when it changes orientation. The rotational diffusion time, \(\tau_r = 4\pi a^2/k_B T\), controls the changes in the orientation of the sphere, and is defined via the orientation autocorrelation function: \(\langle \mathbf{n}(t) \cdot \mathbf{n}(0) \rangle = e^{-t/\tau_r}\).

Finally, the hydrodynamic time that controls the crossover between the inertial and the viscous regimes is given as \(\tau_h = R^2/\nu\), where \(\nu = \eta/\rho\) is the kinematic viscosity of water that involves the mass density \(\rho\). Practically speaking, we always have \(\tau_h \ll \tau_d \ll \tau_r\), although this is not a fundamental requirement.

We can identify three distinct contributions to the velocity autocorrelation function: (1) a contribution from the density fluctuations, which turns out to be only sensitive to the overall symmetric component of the activity and is present even for non-propelled active colloids, (2) a contribution from the asymmetric component of the activity, and (3) a hydrodynamic contribution that entails the passive diffusion of the colloid and the hydrodynamic long-time tail. These will lead to distinct contributions to the mean-squared displacement, which will add up to make the total mean-squared displacement, namely \(\Delta L^2(t) = \Delta L^2_{\text{sym}}(t) + \Delta L^2_{\text{asym}}(t) + \Delta L^2_{\text{hyd}}(t)\). We will focus on each of these contributions separately below.

**Symmetric Contribution.** — The density fluctuations that are accounted for by adding a noise term to Eq. 1.
lead to a contribution to the velocity autocorrelation function that is proportional to \(\alpha_0\) \([16]\) — the \(\ell = 0\) coefficient in the expression for \(\alpha(\theta, \phi, t)\) in terms of the spherical harmonics \(\{\alpha_0 = \frac{1}{\pi} \int d\Omega \alpha(\theta, \phi, t)\}\). This means that the contribution by density fluctuations is only sensitive to the mean overall surface activity of the colloid, and not the patterning structures on it. We find the asymptotic behaviors \(A_{\text{asy}}^{\text{uv}}(t) \sim \frac{3\alpha_0 \mu^2}{\pi^2 D^2 R^3} (t/\tau_d)^{-7/2}\) for \(t \ll \tau_d\) and \(A_{\text{asy}}^{\text{uv}}(t) \sim \frac{3\alpha_0 \mu^2}{32\pi^3 D^2 R^3} (t/\tau_d)^{5/2}\) for \(t \gg \tau_d\). We also calculate the contribution of density fluctuations to the mean-squared displacement, which has the asymptotic behaviors of

\[
\Delta L_{\text{asy}}^2(\tau_d) \sim \frac{8\alpha_0 \mu^2}{3\pi D^2 R^3} \tau_d^{3/2}; \quad t \ll \tau_d,
\]

at short times, and

\[
\Delta L_{\text{asy}}^2(\tau_d) \sim \frac{2\alpha_0 \mu^2}{\pi D^2 R^3} \tau; \quad t \gg \tau_d,
\]

at long times, and a smooth crossover between them. Here, \(\alpha_1 = 1.18710\) is a numerical prefactor.

**Asymmetric Contribution.** Without the noise term, we can calculate the propulsion velocity of the colloid as a function of time for a given time dependent orientation trajectory. We find \(v(t) = v_0 \int_{-\infty}^{\infty} dt' M(t-t')n(t')\), where \(v_0 = -\alpha_1 \mu / (3D)\) is the mean propulsion velocity, \([6]\), and the memory kernel is given as \(M(t) = \frac{3}{4} \int_{-\infty}^{\infty} dt u(t/\tau_d) e^{-u(t/\tau_d)}\), with asymptotic behaviors \(M(t) \sim \frac{3}{2\pi}(t/\tau_d)^{-3/2}\) for \(t \ll \tau_d\) and \(M(t) \sim \frac{1}{2\pi}(t/\tau_d)^{-5/2}\) for \(t \gg \tau_d\). Note that the propulsion velocity is controlled by the \(\ell = 1\) term \((\alpha_1)\) in the surface activity profile.

Rotational diffusion of the colloid randomizes its orientation over the time scale \(\tau_r\), which leads to a contribution to the velocity autocorrelation function of the form of a convolution between two memory kernels and the orientation autocorrelation function. This leads to a velocity autocorrelation function \([17]\) which have three different regimes, due to the presence of two characteristic time scales \(\tau_d\) and \(\tau_r\). At short times, \(t \ll \tau_d \ll \tau_r\), we find

\[
A_{\text{asy}}^{\text{uv}} \sim v_0^2 \left[ 1 - \frac{4c_2}{3} \tau_d \tau_r - \frac{3}{2} \tau_d^{3/2} \tau + \frac{4}{\pi} \frac{t^2}{\tau_d \tau} \ln \left( \frac{t}{\tau_d} \right) \right]
\]

where \(c_2 = 0.642699\) is a numerical prefactor, which implies that the autocorrelation function will be rounded off at small \(t\). For intermediate time, \(\tau_d \ll t \ll \tau_r\), we find

\[
A_{\text{asy}}^{\text{uv}} \sim v_0^2 \left[ 1 - \frac{t}{\tau_r} - \frac{1}{\sqrt{\pi}} \frac{t^{3/2}}{\tau_r^{1/2}} \right]
\]

for short times, \(\tau_d \ll \tau_r \ll t\), we find

\[
A_{\text{asy}}^{\text{uv}} \sim v_0^2 \left[ e^{-t/\tau_r} + \frac{3}{4\sqrt{\pi}} \tau_d^{7/2} \tau_r^{-5/2} \right]
\]

which means that the decay at long times is primarily algebraic and not exponential. Consequently, the mean-squared displacement will have three different regimes. We find the asymptotic form of

\[
\Delta L_{\text{asy}}^2(\tau_d) \sim v_0^2 \tau_d \frac{3}{\tau_r}; \quad t \ll \tau_d \ll \tau_r,
\]

at short times,

\[
\Delta L_{\text{asy}}^2(\tau_d) \sim 2v_0^2 \tau_r; \quad t \sim \tau_r \ll t,
\]

at intermediate times, and

\[
\Delta L_{\text{asy}}^2(\tau_d) \sim 2v_0^2 \tau_r \tau; \quad t \sim \tau_r \ll t,
\]

at long times, with a smooth crossover between them.

**Hydrodynamic Contribution.** Thermal fluctuations of the solvent fluid velocity also contribute to the velocity autocorrelation function of the sphere, because of the no-slip boundary condition between the fluid and the colloid. Performing a similar calculation, one finds \(\Delta L_{\text{hyd}}^2 \sim 6D_0 t^{-2} k_B T \mu^2 / \eta^2 R^3\) \(t^{1/2}\) for \(t \gg \tau_h\), where \(D_0 = k_B T / (6\pi \eta R)\) is the bare diffusion coefficient of the colloid. The first term in the above equation describes the standard passive diffusion of the sphere while the second term corresponds to the hydrodynamic long-time tail \([18, 19]\). At short times when \(t < \tau_h\), one finds \(\Delta L_{\text{hyd}}^2 \sim 3(\frac{3\sqrt{2}}{\pi}) t^2\) where \(M_{\text{eff}}\) is the effective inertial mass of the colloid in water. The above results are summarized in Fig. 1.

**Discussion.** At the longest time scales \((t > \tau_r)\), all of the contributions are diffusive, leading to a total effective diffusion coefficient

\[
D_{\text{eff}} = \frac{k_B T}{6\pi \eta R} + \frac{4\pi \alpha_0^2 \mu^2 \eta R^3}{27 D^2 k_B T} + \frac{c_1 \alpha_0^2 \mu^2}{3\pi^2 D^2 R^2}.
\]

The different terms in the above expression exhibit different \(R\)-dependencies, which causes the asymmetric contribution to be dominant for \(R \gtrsim [D k_B T / (\alpha_1 \mu)]^{1/2}\), while the symmetric contribution takes over when \(R \lesssim c_2^{1/2} \eta^{1/2} / (D^2 k_B T)\). At the shortest time scales, on the other hand, the contribution due to phoretic effects will also be dominated by inertial effects that should lead to ballistic contributions (see Fig. 1).

In the intermediate times, we observe a number of anomalous behaviors. For symmetric active colloids, the super-diffusive \(t^{1/2}\) behavior \([17]\) for \(\tau_h < t < \tau_d\) is a new regime (for isolated self-propelled particles) where the motion is neither ballistic nor diffusive. The reason a symmetric particle can move at all is because density fluctuations of the cloud of solute particles can instantaneously produce an asymmetric distribution and therefore a net propulsion in some direction. This motion, however, will be decorrelated via density fluctuations themselves, leading to fluctuations without symmetry breaking. We can understand the form of Eq. \([20]\) as follows: using \(\Delta L^2 \sim v^2 t^2\), and putting \(v \sim \mu \sqrt{C/R} \sim \mu \delta C/R\), we find \(\Delta L^2 \sim \mu^2 (\delta C(t) \delta C(0))^2 / R^2\). The density auto-correlation function can be written as \(\langle \delta C(t) \delta C(0) \rangle = \langle \delta C^2 \rangle k(t)\), involving the density fluctuations \(\delta C^2\) and the kernel \(k(t)\) that controls the relevant relaxation mode \([20]\). Here, relaxation is controlled by

\[\text{Eq. (1)}\]

\[\text{Eq. (2)}\]

\[\text{Eq. (3)}\]

\[\text{Eq. (4)}\]

\[\text{Eq. (5)}\]

\[\text{Eq. (6)}\]
diffusion, hence $k(t) \sim 1/(Dt)^{3/2}$, and the number fluctuations are controlled by the average number of particles $(\delta N^2) \sim N_{\text{ave}}$—as inherent to any Poisson process—that yield $\langle \delta C^2 \rangle \sim C_{\text{ave}}$. On the other hand, the average density is controlled by the average particle production rate (per unit area) $a_0$ as $C_{\text{ave}} \sim (a_0R^2t)/R^3$. Putting these all together, we find Eq. (2). This shows that the active velocity fluctuations are controlled by two mechanisms: particle production (that controls the density fluctuations) and diffusion of the produced particles. Interestingly, a similar $t^{3/2}$ power law has been observed in the motion of passive tracer particles in a bath of bacteria whose flagella stir up the fluid (and theoretically accounted for using a phenomenological continuum active medium theory) \cite{12}, and in ion channel gating \cite{21}, both of which cases are also governed by some sort of density fluctuations \cite{22}.

For asymmetric particles when $\tau_h < t < \tau_d$, the $t^{3/2}$ contribution is added (with a positive coefficient) to the $t^2$ propulsive term. On the other hand, for $\tau_d < t < \tau_r$ the memory effect that exists for self-propelled asymmetric colloids introduces an anomalous anti-correlation (i.e. contribution with negative sign) in the velocity autocorrelation function and the mean-squared displacement [Eq. (3)]. Such anomalous corrections, which have also been observed in continuum theories of interacting active self-propelled particles \cite{11}, are reminiscent of the effect of the hydrodynamic long-time tail. Note, however, that the anomalous $-\tau^{3/2}$ correction in Eq. (4) corresponds to much longer time scales and should be more easily observable than the hydrodynamic long-time tail.

To get a better feel for the working domain of each regime, we can write the time scales (for water at room temperature and using a typical value of $a = 1 \AA$) in the following convenient form: $\tau_h = 10^{-6} (R/1\mu m)^2 s$, $\tau_d = 10^{-3} (R/1\mu m)^2 s$, and $\tau_r = 3 (R/1\mu m)^3 s$. This shows that while rapid cameras or scattering techniques \cite{12,14} could in principle resolve all the three domains for micron-sized beads, using $R = 20 \mu m$ (which yields $\tau_d = 0.4 s$ and $\tau_r = 2.4 \times 10^4 s$) should provide a comfortable working range for an experiment that aims to resolve the anomalous components of the motion. Finally, we note that here we have only focused on the phoretic contributions to velocity fluctuations, and in practice other sources of fluctuations might also be present \cite{10}, which need to be taken into account.

In summary, we have shown that active colloidal particles that interact with their self-generated cloud of solute particles can have a range of different types of stochastic motions. Using parameters such as surface activity, surface mobility, and size, we can tune the behavior of active colloidal particles, and this could provide new possibilities in designing functional motile agents for applications in micro- and nano-fluidics and targeted delivery.

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\* Electronic address: r.golestanian@sheffield.ac.uk

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