BROWNIAN MOTION OF LOW SYMMETRY COLLIDAL PARTICLES

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by

Ayan Chakrabarty

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Dissertation written by
Ayan Chakrabarty
B.Sc, Calcutta University, Kolkata, India, 2005
M.Sc, Indian Institute of Technology, Kanpur, India, 2007
Ph.D, Kent State University, Kent, U.S.A. 2014

Approved by

Dr. Qi-Huo Wei, Chair, Doctoral Dissertation Committee
Dr. Satyendra Kumar, Co-Advisors, Doctoral Dissertation Committee
Dr. Jonathan V. Selinger
Dr. Hamza Balci, Members, Doctoral Dissertation Committee
Dr. Elizabeth Mann
Dr. Robin Selinger

Accepted by

Dr. Jim Gleeson, Chair, Department of Physics
Dr. Janis Crowther, Associate Dean, College of Arts and Sciences
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DEDICATION

Dedicated to

My loving parents Dr. Ranajit Chakrabarty & Sipra Chakrabarty
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Kent, Ohio.

U.S.A.
CHAPTER 1

INTRODUCTION TO BROWNIAN MOTION

At microscopic scales, the motion of particles is driven primarily by the erratic forces exerted by the surrounding molecules due to thermal fluctuations, a phenomenon known as Brownian motion. Brownian motion was first discovered by the botanist Robert Brown in 1857 when he observed under the microscope the incessant and erratic motion of the pollen grains suspended in water. He found that other mineral particles showed similar behavior in all kinds of fluids and came to the conclusion that the particles are ‘living’. M. Gouy in 1888 showed the dependence of the motion on the viscosity of the fluid. Independent studies by Exner in 1900 showed the effects of particle size and temperature of the liquid on its movement. Einstein in 1905 first explained the phenomena as the bombardments of the lighter solvent molecules on the Brownian particle [1]. M. Smoluchowski in a similar approach independently described Brownian motion in 1906. Perrin in 1908 experimentally verified Einstein’s theory and proved the existence of atoms and molecules [2].

Einstein’s theory also established that the Brownian motion is a general phenomenon of diffusive processes [1]. Since then its rich physics and critical roles in various biological, chemical, physical and financial systems have inspired extensive research over the past century [3-13]. Recent advances in experimental techniques have not only revealed various fundamental aspects of Brownian motion [6-12] but also led to new applications such as microrheology [14-17] and particle and molecular separation based on Brownian ratchets [18-20].
1.1 Brownian Motion as a Diffusive Process

Diffusion is a transport process by which small particles spontaneously translate, rotate and evolve towards an isotropic distribution without external forces. It is ubiquitous in nature and the key mechanism for reaction kinetics of molecules, biological processes, transport of heat and electricity, crystal nucleation and growth. Therefore predicting and understanding the diffusion coefficients of rigid particles suspended in a continuum medium is of practical and theoretical importance.

Transport phenomena follow the laws of conservation of mass. The conservation of physical quantities like mass, charge or energy can be described by the continuity equation

\[
\frac{\partial \rho(x,t)}{\partial t} = -\nabla \cdot \vec{j}
\]  
(1.1)

where \( \rho \) is the density or concentration. \( \vec{j} \) is the current or flux through a unit area. Now, if there is a concentration gradient then the current is given by the Fick’s law

\[
\vec{j} = -D \nabla \rho(x,t)
\]  
(1.2)

where D is the diffusion coefficient. Combining Eq. (1.1) and (1.2) yields the diffusion equation

\[
\frac{\partial \rho(x,t)}{\partial t} = -D \nabla^2 \rho(x,t)
\]  
(1.3)

The solution of the diffusion equation gives the distribution of the diffusing particles or molecules as a function of space and time.

The motion of Brownian particles suspended in water, is random and two consecutive displacement steps are mutually independent. In another word, the particle
motions in nearest neighboring time intervals ($\tau$) are uncorrelated. Following Einstein’s derivation, let the number of suspended particles be $n$ and in the time interval $\tau$ the displacement step taken by each particles be $\xi$. If $\psi(\xi)$ is the probability that a particle will execute a jump of $\xi$ then the probability that $dn$ numbers of particles will execute a jump between $\xi$ and $\xi + d\xi$ is defined as:

$$\frac{dn}{n} = \psi(\xi)d\xi$$

and the total probability of the jump is given by:

$$\int_{-\infty}^{\infty} \psi(\xi)d\xi = 1$$

($1.4$)

($1.5$)

$\psi(\xi)$ should satisfies the condition

$$\psi(\xi) = \psi(-\xi)$$

($1.6$)

For a one dimensional problem, the density of the Brownian particles $\rho(x, t + \tau)$ at time $t + \tau$ is given by

$$\rho(x, t + \tau) = \int_{-\infty}^{\infty} \rho(x + \xi, t)\psi(\xi)d\xi$$

($1.7$)

$\rho(x + \xi, t)$ is the density at time $t$ and the integration is over all possible jumps from $x + \xi$ to $x$ with probability $\psi(\xi)$ . Therefore for small time steps we have:

$$\rho(x, t + \tau) = \rho(x, t) + \tau \frac{\partial \rho}{\partial t}$$

($1.8$)

Similarly, for a small jump size $\xi$ we can expand $\rho(x + \xi, t)$ as:
\[ \rho(x + \xi, t) = \rho(x, t) + \xi \frac{\partial \rho(x, t)}{\partial x} + \frac{\xi^2}{2!} \frac{\partial^2 \rho(x, t)}{\partial^2 x} + \ldots \]  
(1.9)

Therefore, using Eq. (1.8) and (1.9) we can write Eq. (1.7) as:

\[
\rho(x, t) + \tau \frac{\partial \rho(x, t)}{\partial t} = \int_{-\infty}^{+\infty} \rho(x, t)\psi(\xi)d\xi + \int_{-\infty}^{+\infty} \left( \frac{\partial \rho(x, t)}{\partial x} \right) \xi \psi(\xi)d\xi \\
+ \int_{-\infty}^{+\infty} \left( \frac{\partial^2 \rho(x, t)}{\partial^2 x} \right) \frac{\xi^2}{2!} \psi(\xi)d\xi + \ldots
\]
(1.10)

Considering that \( \psi(\xi) \) is an even function and \( \int_{-\infty}^{+\infty} \psi(\xi)d\xi = 1 \), Eq. (1.10) can be simplified as:

\[
\frac{\partial \rho(x, t)}{\partial t} = \frac{1}{\tau} \left[ \int_{-\infty}^{+\infty} \frac{\xi^2}{2!} \psi(\xi)d\xi \right] \frac{\partial^2 \rho(x, t)}{\partial^2 x}
\]
(1.11)

Putting \( D = \frac{1}{\tau} \left[ \int_{-\infty}^{+\infty} \frac{\xi^2}{2!} \psi(\xi)d\xi \right] \), we obtain

\[
\frac{\partial \rho(x, t)}{\partial t} = D \frac{\partial^2 \rho(x, t)}{\partial^2 x}
\]
(1.12)

Eq. (1.3) and Eq. (1.12) show that the equation for the density of a Brownian particles and is same as the diffusion equation. The solution of the diffusion equation at the instant of time \( t \) is given by

\[
\rho(x, t) = \frac{1}{\sqrt{4\pi D t}} e^{-\frac{x^2}{4Dt}}
\]
(1.13)

Eq. (1.13) implies that the distribution is Gaussian with a zero mean therefore the Brownian particle on an average remains at the same place (Figure 1.1.1) which is a
Figure 1.1.1 Trajectories of mastic spheres suspended in water, observed by F. Perrin.

The square grid in A is 3 µm, and the spheres are 0.53µm in radius [2].
signature of random walk. The probability $P(x, t)$ of finding the particle at some location is proportional to its local density $\rho(x,t)$. Hence,

$$P(x,t) = Const. \times \rho(x,t)$$

(1.14)

Therefore, the mean square displacements are given by

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 P(x,t) dx = 2Dt$$

(1.15)

which are linearly proportional to the time with the proportionality constant being the diffusion coefficient of the particle.

### 1.2 Langevin Formalism

Einstein in 1905 established the expression for the mean square displacements which can be directly measured and verified in experiments. J. Perrin conclusively verified this prediction in 1908 in his experiments and wrote “it becomes rather difficult to deny the objective reality of molecules”. Paul Langevin came to the same conclusion in 1908 using a completely different approach. He applied Newton’s second law to derive a mathematical description of Brownian trajectories. While Einstein’s description included the time evolution of the probability distribution of the Brownian particles, Langevin used a generalized form of the Newton’s mechanical equations to derive a set of stochastic differential equations to describe the Brownian motion. In its phenomenological form the perpetual erratic motion of a micron sized particle perceived under the microscope is due to the random bombardment of the solvent molecules. As shown in [Figure 1.2.1] the suspended particle which is very large on a molecular scale suffers as many as approximately $10^{21}$ collisions per second in arbitrary direction by the
Figure 1.2.1 Schematic of a Brownian particle suspended in fluid. The size of the fluid molecules is three to four orders of magnitude smaller than the Brownian particle.
solvent molecules. Therefore description of a single collision is inconsequential and a stochastic analysis of the system is required which determines the average effect on the Brownian particle due to the collision with the fluid molecules.

1.2.1 Langevin Equation

For simplicity a one dimensional model will be considered. The Brownian particle experiences two forces: a random force $f(t)$ due to the irregular bombardment of the solvent molecules, and an average drag force $F_{\text{drag}}$ which is proportional to the velocity through the Stokes law $F_{\text{drag}} = -\gamma \frac{dx}{dt}$. Here $\gamma$ is the hydrodynamic friction coefficient. The Newton’s second law can be written as

$$ m \frac{d^2x}{dt^2} = -\gamma \frac{dx}{dt} + f(t) \quad (1.16) $$

This stochastic differential equation captures the whole physical picture of the Brownian motion in a fluid.

1.2.2 Stochastic Forces

For a stationary Brownian particle in a fluid, the fluctuating forces should satisfy the condition that the average velocity of the particle goes to zero. To comply with this condition the random force should satisfy

$$ \langle f(t) \rangle = 0 \quad (1.17) $$

Here the average is over the ensembles of suspended Brownian particles which are in equilibrium and have the same initial condition.
Secondly, the consecutive displacements should be uncorrelated. This implies that the random force $f(t)$ should vary much rapidly compared to the velocity of the particle. Therefore, during a time interval $\Delta t$, the force $f(t)$ should fluctuate several times but the change in the velocity is very small. Hence the correlation function $\langle f(t) f(t') \rangle$ should have a maximum at time $t=t'$ and falls off to zero for time $|t-t'| > \tau_c$ where $\tau_c$ is the correlation time and depends on the damping constant. More detail discussions on the time scales will be done later. Given that the time intervals for experiments are much larger than the average collision time $\tau_c$, the random forces should satisfy:

$$\langle f(t) f(t') \rangle = A \delta(t-t')$$

(1.18)

The random forces are assumed to be a white noise, that is, they follow a Gaussian distribution. The constant $A$ is determined using the first two moments Eq. (1.17) and (1.18) of the random force and the Equipartition theorem which relates the momentum $p(t)$ of the particle with its thermal energy.

### 1.2.3 Solution of Langevin Equation in 1D

The average kinetic energy of Brownian particles in 1D is given by

$$\left\langle \frac{1}{2} m \left( \frac{dx}{dt} \right)^2 \right\rangle = \frac{1}{2} k_B T$$

(1.19)

where $m$ is the mass and $k_B$ is the Boltzmann constant and $T$ is the absolute temperature.

Using Fourier transform for the position $x(t)$ and force $f(t)$ we have
Substituting them into Langevin equation (1.16) yields:

\[
mx(\omega)[-\omega^2] = -\gamma \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} x(\omega)[-i\omega] e^{-i\omega t} + \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} f(\omega) e^{-i\omega t}
\]

\[
m\int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} x(\omega)[-\omega^2] = -\gamma \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} x(\omega)[-i\omega] e^{-i\omega t} + f(\omega)
\]

Hence,

\[
x(\omega) = \frac{f(\omega)}{-m\omega^2 - i\omega\gamma}
\]

Therefore from (1.19) we have the average kinetic energy of the Brownian particles

\[
\langle K.E. \rangle = \left\langle \frac{1}{2} m \left( \frac{dx}{dt} \right)^2 \right\rangle
\]

\[
\langle K.E. \rangle = \frac{1}{2} m \left\langle \left( \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} x(\omega)[-i\omega] e^{-i\omega t} \right) \times \left( \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} x(\omega')[-i\omega'] e^{-i\omega' t} \right) \right\rangle
\]

\[
\langle K.E. \rangle = \frac{1}{2} m \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} (\omega\omega') e^{-i\omega t - i\omega' t} \langle x(\omega) x(\omega') \rangle
\]

Using Eq. (1.24) we can write
\[ \langle K.E. \rangle = \frac{1}{2} m \int_{-\pi}^{\pi} \frac{d\omega}{2\pi} \int_{-\pi}^{\pi} \frac{d\omega}{2\pi} (\omega \omega') e^{-i\omega t - i\omega' t} \times \left( \frac{f(\omega)}{-m\omega^2 - i\omega \gamma} \times \frac{f(\omega')}{-m\omega'^2 - i\omega' \gamma} \right) \]

which can be simplified as

\[ \langle K.E. \rangle = \frac{1}{2} m \int_{-\pi}^{\pi} \frac{d\omega}{2\pi} \int_{-\pi}^{\pi} \frac{d\omega}{2\pi} e^{-i\omega t - i\omega' t} \times \frac{(\omega \omega')}{(-m\omega^2 - i\omega \gamma)(-m\omega'^2 - i\omega' \gamma)} \langle f(\omega)f(\omega') \rangle \]

From Eq. (1.21) we can write

\[ \langle f(\omega)f(\omega') \rangle = \left\{ \int_{-\infty}^{\infty} dt e^{i\alpha t} \int_{-\infty}^{\infty} dt' e^{i\alpha t'} \right\} \]

\[ = \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' e^{i\alpha t} \langle f(t)f(t') \rangle \]  \hspace{1cm} (1.30)

Using Eq. (1.18) leads to:

\[ \langle f(\omega)f(\omega') \rangle = 2\pi \Delta \delta(\omega + \omega') \]  \hspace{1cm} (1.31)

Therefore the kinetic energy Eq. (1.29) can be expressed as:

\[ \langle K.E. \rangle = \frac{1}{2} m \int_{-\pi}^{\pi} \frac{d\omega}{2\pi} \int_{-\pi}^{\pi} \frac{d\omega}{2\pi} e^{-i\omega t - i\omega' t} \times \frac{(\omega \omega')}{(-m\omega^2 - i\omega \gamma)(-m\omega'^2 - i\omega' \gamma)} 2\pi \Delta \delta(\omega + \omega') \]  \hspace{1cm} (1.32)

or

\[ \langle K.E. \rangle = \frac{1}{2} mA \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{1}{m^2 \omega^2 + \gamma^2} = \frac{A}{4\gamma} \]  \hspace{1cm} (1.33)

Considering Eq. (1.19), we obtain

\[ A = 2\gamma k_B T \]  \hspace{1cm} (1.34)

Substituting it into Eq. (1.18) gives:
The mean square displacement is given by \( \langle (x(t) - x(0))^2 \rangle \) where \( x(t) \) is the position of the Brownian particles at time \( t \) and \( x(0) \) is the initial position at time \( t=0 \).

Using Eq. (1.20) we have

\[
\langle (x(t) - x(0))^2 \rangle = \left( \int_{-\pi}^{+\pi} \frac{d\omega}{2\pi} x(\omega) \left[ e^{-i\omega t} - e^{-i\omega 0} \right] \right)^2
\]

which can be rewritten as:

\[
\langle (x(t) - x(0))^2 \rangle = \int_{-\pi}^{+\pi} \frac{d\omega}{2\pi} \int_{-\pi}^{+\pi} \frac{d\omega'}{2\pi} (e^{-i\omega t} - 1)(e^{-i\omega' t} - 1) x(\omega) x(\omega')
\]

(1.36)

Combining Eq. (1.24) and Eq. (1.31) yields:

\[
\langle x(\omega) x(\omega') \rangle = \frac{2\pi \Lambda \delta(\omega + \omega')}{(-\omega^2 - i\omega \gamma)(-\omega'^2 - i\omega' \gamma)}
\]

(1.37)

Substituting Eq. (1.37) in Eq. (1.36) gives

\[
\langle (x(t) - x(0))^2 \rangle = \Lambda \int_{-\pi}^{+\pi} \frac{d\omega}{2\pi} \frac{e^{-i\omega t} - 1}{m^2 \omega^4 + \omega^2 \gamma^2} \left( e^{i\omega t} - 1 \right) = \Lambda \int_{-\pi}^{+\pi} \frac{d\omega}{2\pi} \frac{2 - 2 \cos \omega t}{m^2 \omega^4 + \omega^2 \gamma^2}
\]

or:

\[
\langle (x(t) - x(0))^2 \rangle = 2k_B T \frac{m}{\gamma} \frac{-\gamma \bar{p}}{-1 + e^{-m \gamma}} + |\bar{p}|
\]

(1.39)
1.2.4 Time Scales

Molecular Collision Time

For the solvent in which the Brownian particle is suspended, the molecules are closely packed and encounter a collision with each other or with the colloid particle after traversing approximately a distance equivalent to its own radius. In 1D the velocity of the solvent molecules is obtained from the Equipartition theorem as \( v = \sqrt{\frac{k_B T}{m}} \) and \( m \) is the mass of each solvent molecule. If \( a \) is the radius of the solvent molecules the collision time \( \tau_c \) is of the order of \( \tau_c \sim \frac{a}{\sqrt{k_B T/m}} \). We can do an order of estimate calculation by putting \( a \sim 1\text{Å} \) and \( v \sim 370 \text{ m/sec} \) and obtain the characteristic collision time as \( \tau_c \sim 10^{-13} \) sec. Therefore the Brownian particle can be taken as completely stationary at these time scales and for \( t >> \tau_c \) it experience a continuous fluid rather than individual kicks from the solvent molecules.

Momentum Relaxation Time \( \tau_m \)

The momentum relaxation time is defined as the time taken by the colloidal particle to lose its momentum \( \vec{p}_0 = m\vec{v}_0 \) due to the viscous energy dissipation at the time scale \( t >> \tau_c \). \( \vec{p}_0 \) is the momentum at time \( t=0 \). The viscous force is proportional to the velocity of the colloid: \( \vec{F}_{drag} = -\gamma \vec{v} \). Therefore using Newton’s second law we have
The solution of Eq. (1.40) is given by
\[ \ddot{v}(t) = -\gamma \dot{v} \]
where \( \tau_m = m/\gamma \) is the characteristic momentum relaxation time. For a spherical particle the hydrodynamic resistance \( \gamma \) is given by \( \gamma = 6\pi\eta r \), where \( \eta \) is the viscosity of the solvent and \( r \) is the radius of the colloidal particle. A simple estimation can show that for a micron sized particle in water, \( \tau_m \approx 10^{-7} \) sec.

**Ballistic Time Scales**

Putting \( \tau_m = m/\gamma \) in Eq. (1.39), we can expand the exponential term for \( t \ll \tau_m \):

\[
\left\langle (x(t) - x(0))^2 \right\rangle = k_B T \frac{\gamma_m}{\gamma^2} \left[ 1 + 1 - \frac{|t|}{\tau_m} + \frac{t^2}{2\tau_m^2} \right] + |t|
\]

or

\[
\left\langle (x(t) - x(0))^2 \right\rangle \approx \frac{k_B T r^2}{m} \approx \left\langle v^2 \right\rangle t^2
\]

Therefore at time scales much smaller than momentum relaxation time, the Brownian particle exchanges kinetic energy with the surrounding solvent molecules while undergoing a ballistic motion, and the displacements are proportional to the time.

**Brownian or Diffusive Time Scale**

At time scale much larger than the momentum relaxation time \( t \gg \tau_m \) the Eq. (1.39) can be simplified as
\[
\langle (x(t) - x(0))^2 \rangle \approx \frac{A t}{\gamma^2} \approx 2 \left( \frac{k_B T}{\gamma} \right) t \approx 2D_t t
\]  

(1.42)

where

\[
D = \frac{k_B T}{\gamma}
\]  

(1.43)

is the diffusion coefficient. Eq. (1.43) is known as Stoke-Einstein relation. Therefore the displacement of the particle is proportional to the square root of the time, a characteristic of Brownian motion. It is important to note that in the diffusive regime the displacements are independent of the mass of the particles due to successive momentum exchanges with the solvent molecules. In other words, the particle is over-damped and the drag force completely dominates over the inertial force.

For the rotational Brownian motion the diffusion coefficients can be similarly derived with the forces replaced by torques and the translational drag by rotational drag. For a spherical particle the hydrodynamic rotational resistance is given by \( \gamma_{rot} = 8\pi\eta r^3 \); the rotational diffusion coefficient can be obtained using the Stokes-Einstein relation:

\[
D_\theta = D_{rot} = \frac{k_B T}{\gamma_{rot}} = \frac{k_B T}{8\pi\eta r^3}
\]  

(1.44)

and the mean square angular displacement is given by \( \langle \theta^2 (t) \rangle = 2D_\theta t \).

### 1.3 Brownian Motion of Low Symmetry Colloids

For low symmetry particles, the hydrodynamic frictional forces experienced by the Brownian particle will not be isotropic. As the effective length \( l \) of the particles increases the rotational diffusion coefficient goes down as \( l^3 \) while the translational
diffusion coefficients go down only as $t^1$. Therefore it can be understood that as the diffusion proceeds, the displacement along the long axis dominates that along the short axis. This tendency is, however, opposed by rotational diffusion. As suggested by F. Perrin [21, 22], particle anisotropy leads to dissipative coupling of translational motion with that of the rotational motion.

For an arbitrary shaped particle, the hydrodynamic drag force $\mathbf{F}_{\text{drag}}$ and torque $\tau_{\text{drag}}$ are linearly proportional to the translational velocity ($v$) and rotational angular velocity ($\omega$):

$$
\begin{pmatrix}
\mathbf{F}_{\text{drag}} \\
\tau_{\text{drag}}
\end{pmatrix} = -
\begin{pmatrix}
\gamma^T & \gamma^C_P \\
\gamma^C_P & \gamma^R_P
\end{pmatrix}
\begin{pmatrix}
v \\
\omega
\end{pmatrix}
$$

(1.45)

The proportionality is the hydrodynamic resistance matrix $\gamma = \begin{pmatrix}
\gamma^T & \gamma^C_P \\
\gamma^C_P & \gamma^R_P
\end{pmatrix}$ with respect to a tracking point $P$ fixed to the particle. For motion in three dimensions, $\gamma$ is a 6×6 tensor. $\gamma^T$, $\gamma^R_P$, $\gamma^C_P$ are the 3×3 translational, rotational and coupling resistance sub-matrices respectively. $\gamma^C_P$ is the transpose of the coupled hydrodynamic resistance sub matrix. $\gamma^R_P$ and $\gamma^C_P$ depend on the origin of the coordinate system hence denoted by the subscript $P$ while $\gamma^T$ is independent of the origin. The translational and rotational resistance sub-matrices are in general symmetric and the off-diagonal terms go to zero in some specific coordinate system for bodies with symmetry. On the contrary the resistance sub-matrix is in general asymmetric.
The diffusion tensor is inversely proportional to the hydrodynamic resistance and is given by the generalized Stokes-Einstein relationship:

\[ D_{ij} = \begin{pmatrix} D^T & D^C \\ D^C & D^R \end{pmatrix} = \frac{k_B T}{\gamma_{ij}} \]  

(1.46)

\( D^T \) and \( D^R \) are the 3×3 translational and rotational diffusion sub-matrices in three dimensions. \( D^C \) is the coupled diffusion sub-matrix due to the translation and rotation coupling and \( D^C \) is the transpose.

1.3.1 Hydrodynamic Centers

Brenner and others showed [23-28] that the 3×3 translational and rotational sub-matrices for motion in three dimensions are symmetric in general but the coupling matrix is in general non-symmetric. However for all particles, there exists one unique point, called the Center of Reaction (CoR), at which the coupling hydrodynamic resistance matrix can be shown to be symmetric; there exists another unique point, called the Center of Diffusion (CoD), at which the coupling diffusion matrix becomes symmetric. The trace of the translational diffusion tensor is minimal at the CoD. In general the CoR and CoD do not coincide with each other and do not overlap with the center-of-mass. However for bodies with special geometric symmetries there exists a special point called the Center of Hydrodynamic Stress (CoH) where the coupled resistance matrix goes to zero and the CoD and the CoR coincide.

1.3.2 Diffusion Coefficients

From Eq. (1.46) the 3×3 diffusion sub-matrices can be derived as [27]:

\[ 17 \]
At Center of Reaction the coupling resistance matrix $\gamma_p^C$ is symmetric and at the CoH $\gamma_p^C = 0$. It can be seen from Eq. (1.49) that the coupling diffusion matrix $D^C$ also goes to zero at the CoH. Therefore for bodies which have a CoH, the translational and rotational motion is decoupled at this point.

Particles which possess a CoH are called non-skewed. Brenner [24] showed that for motion in three dimensions, such particles need to have three mutually perpendicular planes of symmetry. On the contrary, for skewed bodies which possess two or fewer planes of symmetry including bodies with helicoidal symmetry, there exists no CoH; the translation and rotation are intrinsically coupled. The coupled diffusion matrix is needed to describe the Brownian motion.

1.4 Motivations and Brief Summary of the Dissertation

Colloids with anisotropic shapes and interactions are emerging as a topic of many studies owing to their potential applications as building blocks for self-assembling new structures and materials [29-32]. Innovative chemical synthesis and micro-fabrication methods have enabled productions of colloids with a variety of exotic shapes such as Janus, patchy, and lock-key particles [33-37]. Janus particles with half hydrophobic and half hydrophilic surfaces aggregate into highly ordered structures [38], and triblock Janus particles self-assemble into more complex structures such as Kagome lattices [39-40].
Patchy colloidal particles enables site-specific directional interactions, allowing for assembly of complex structures such as colloidal micelles [40] and mimicking valence bonding of molecular systems [42]. By using complementary particle shapes and depletion forces, lock-key type of colloidal systems can form flexible dimeric, trimeric, tetrameric colloidal molecules and colloidal polymers [43]. The ability to engineer geometric shapes and patterned surface chemistry of individual colloidal particles has opened a new horizon towards programmable and directed colloidal self-assembly.

While hydrodynamic theories have been developed by Brenner and others about 50 years ago for the Brownian motion of irregularly-shaped bodies [23-28], experimental studies of anisotropic colloidal particles remain rarely explored [6, 44-46]. For example, video microscopic and theoretical studies of ellipsoidal particles have demonstrated that the translation-rotation coupling makes the displacement probability distribution functions (PDF) non-Gaussian although such coupling disappears in the body-moving frame [6]. The Brownian motion of more complex geometric shapes has been realized by using aggregates of spherical particles [47-52]. It has also been shown that the hydrodynamics of anisotropic particles is important to the motion of self-propelled particles and can be readily designed to yield different types of motion trajectories [53-55].

In this dissertation we study the Brownian motion of boomerang-shaped colloidal particles under quasi two-dimensional confinements. The symmetric boomerang particles with $C_{2v}$ mirror symmetry represent an attractive system for studying the Brownian motion of low symmetry particles because their CoM and CoH do not coincide and both
lie outside the body. Especially, the location of the CoH is unknown before the motion of any tracking point (TP) is analyzed. By designing boomerangs with asymmetric arm lengths, we can easily realize a model particle system with no symmetry to represent particles with arbitrary shapes in a 2D system.

Our research of Brownian motion has been focused on individual boomerang particles and thus ultra-low concentrations of particles are used to ensure no hydrodynamic interactions exist between particles. It can be expected that the dispersions of boomerang colloids can be easily extended to high concentrations as a model system for liquid crystals. Especially biaxial-nematic ordering of bent-core liquid crystal molecules [56-57, 88-89] has been an elusive and debated topic in the liquid crystal community. Colloidal systems formed from boomerang shaped particles mimicking the bent-core liquid crystal molecules would be an ideal platform to study their phases at single particle resolution.

The dissertation contains four parts and organized as the following: Chapter 2 describes the methods for fabrication of boomerang particles with different arm lengths and apex angle. Video microscopy technique and single particle tracking algorithms that was developed to study the diffusion of boomerangs in a quasi-two dimensional geometry has been outlined. Chapter 3 describes experimental and theoretical study of the Brownian motion of symmetric boomerang particles with equal arms. Symmetric boomerangs with different apex angles have been studied and their diffusion coefficient as a function of the apex angles is compared. In Chapter 4 we study the non-Gaussian displacement probability distribution function due to translation-rotation coupling of the
boomerang particles. Translation-rotation coupling as a function of tracking point and its effects on the displacement probability distribution has been illustrated. Chapter 5 describes the Brownian motion of asymmetric boomerangs i.e. boomerangs with unequal arms. Asymmetric boomerangs with no planes of symmetry in two dimensions represent class of rigid bodies of most general shapes. Therefore our experimental and theoretical study of the Brownian motion of asymmetric boomerangs completes the understanding of the motion of low symmetry particles in two dimensions. Chapter 6 is summary and conclusion.
CHAPTER 2

EXPERIMENTAL METHODS

2.1 Introduction

In this chapter we will present the fabrication steps of the boomerang colloidal particles which represent a class of rigid bodies of reduced symmetry. As no software is commercially available for tracking asymmetric particles, we will develop our own tracking algorithm to obtain the position and orientation of the boomerang particles as a function of time in a quasi-two dimensional geometry. The normal tracking algorithm based on intensity weighted center-of-mass does not yield high precision for the boomerangs since some out-of-plane rotational motion causes uneven intensities for the two arms and affect the accuracy in locating the center of mass.

2.2 Micro-fabrication of Boomerang Particles

To fabricate boomerang shaped colloidal particles, we developed a fabrication procedure based on photolithography as reported in the literature [58]. The process flow for fabrication is shown in [Figure 2.2.1]. In the first step a 17 nm thick sacrificial layer (Omnicoat, a dissolvable polymer, Microchem Inc.) is first spin coated on a silicon wafer. It was followed by spin coating a ~500nm UV-curable epoxy photoresist SU8 (Microchem Inc.). The SU8 thickness was controlled by varying the solute content of the SU8 solution and also the spin speed. The SU8 layer was patterned by exposing it to UV through a mask by using an autostepper projection photolithography system with a 5x size reduction. The mask defined the boomerang shaped particles with different sizes and
Figure 2.2.1 Process flow for the micro fabrication of the boomerang particle.
apex angles on the SU8 photoresist. Since SU8 is a negative photoresist only the polymer chains in the exposed part get crossed linked and unexposed resists are removed when the wafer is washed with the SU8 developer. These boomerang particles made on Si wafers were released by submerging in the Omnicoat stripper (PG remover, Microchem Inc.). Sonication is used to reduce the release time. SEM pictures of the fabricated symmetric and asymmetric boomerang particles of different sizes and apex angles on the silicon wafer before they are released in the solution are shown in [Figure 2.2.2].

2.3 Particle Stabilization and Cell Assembly

The particles collected from the silicon wafer are in the stripper solution. The stripper solvent was then replaced by deionized water through centrifugation. 1 mM anionic surfactants (SDS) were added into the aqueous particle suspensions to prevent the particles from aggregation.

To confine the particles in quasi-two-dimensional geometries, sample cells composed of two parallel glass slides were used. The cell thicknesses were controlled at about 2 µm by using glass beads as spacers. A dilute dispersion of the colloidal particles was filled in the cells, and particle separations were larger than 100 µm so that no hydrodynamic interactions exist between these particles.

2.4 Video Optical Microscopy

The Brownian motion of the boomerang particles was observed under an inverted transmission bright field optical microscope attached with an electron multiplying charge coupled device (EMCCD, Andor technologies). Videos of single boomerang particles
Figure 2.2.2 SEM pictures of the boomerang particles fabricated on a silicon wafer. (a) Vertex angle: 90°, arm length: 2.33 µm; (b) Vertex angle: 90°, arm length: 1.3 µm short, 2.2 µm long; (c) Vertex angle: 110°, arm length 2.4 µm. (d) Vertex angle: 110°, arm length: 1.3 µm short, 2.4 µm long; (e) Vertex angle: 120°, arm length 2.45 µm. (f) Vertex angle: 120°, arm length: 1.4 µm short, 2.4 µm long. The scale bars are 2 µm.
were taken at a time interval $\tau$ between neighboring frames set at $\tau = 0.05$ s for all the videos.

### 2.4.1 Image Processing Algorithm

A representative optical microscopic image of a boomerang particle is shown in Figure 2.4.1(a). To determine the position and orientation of the boomerang particle, the image processing undergoes the following steps: (i) the gray scale image is inversed [Figure 2.4.1(b)]; (ii) the image is smoothened using a Gaussian filter, and the background intensity is subtracted [Figure 2.4.1(c)]; (iii) the intensity profiles along different directions are scanned to find the points on the central axes of two arms and the cross point of the two central axes [Figure 2.4.1(d)]; (iv) based on the results of the last step, the intensity profile scanning is repeated to refine the particle location and orientation [Figure 2.4.1(e)]. For steps (iii) and (iv), a region of interest around the particle is chosen [see the example in Figure 2.4.1(c)], and our calculations are restricted to this region to substantially reduce the processing time.

As for the image smoothing in step (ii), we used the Gaussian filter, which is especially effective in eliminating high frequency noises that have normal distributions [59]. The intensity value $I_0(x_1, x_2)$ of at pixel $(x_1, x_2)$ is reset as the average of its neighboring pixel intensities weighted by a zero-mean discrete Gaussian function $g(i, j) = exp[-(i^2+j^2)/2\sigma^2]$. The reset value $I(x_1, x_2)$ can be expressed as
Here \( g(i, j) \) is a \((2m+1)\times(2n+1)\) matrix. The degree of smoothing is determined by the standard deviation \( \sigma \). The filter matrix size, i.e. \( 2m+1 \) and \( 2n+1 \), is usually chosen to be 2 to 3 times of \( \sigma \) for reasonable clipping of the Gaussian curve. For our images, we found that \( m = n = 2 \) and \( \sigma = 2 \) give the optimal results. The effectiveness of the smoothing can be seen from the representative pictures before and after the filtering [Figure 2.4.1(b) and (c)].

In step (iii), we firstly find a direction that is approximately parallel to the angle bisector of the boomerang arms. The image is scanned along 10 different directions which are evenly distributed between 0° and 180°. For each scanning direction, the intensities on parallel lines at equally spaced sub-pixel points are calculated through interpolation. Here the spacing between both the scanning lines and the sub-pixel points on these lines are set at 0.5 pixel size. For each scanning line in a given direction, the number of points with intensities above a set threshold is counted as the cross-section length; the maximal cross-section length among these parallel scanning lines is recorded as the cross-section length for that scanning direction. The scanning direction that has the smallest cross-section length is the direction closest to the bisector of the two arms.

With this approximate bisector direction, we proceed to find approximate central axes of the arms. Along equally spaced lines parallel to this direction, the intensities at equally spaced positions are calculated again through linear interpolation [schematic in
Figure 2.4.1(c); the intensity profiles along these lines are fitted with Gaussian functions [Figure 2.4.1(f)]. The peak loci of these Gaussian fittings give the points on the central axes. The spacing between the scanning lines and between the points on these lines are set at 0.5 pixel. These central points close to the arm tips and the apex point are eliminated, and the rest are fitted with linear functions to obtain the central axes of these two arms and then their cross point (i.e. center of the body, CoB) [Figure 2.4.1(d)]. This method of intensity profile fitting with Gaussian functions has been previously used in image processing to find the central axes of ellipsoidal particles [60] and in super-resolution molecular and spherical particle imaging and tracking [61-62]. The Gaussian profile fitting has also been used to analyze the bending dynamics of fluctuating filaments [63].

In step (iv), the bisector line is calculated based on the central axes found in step (iii). The image is split into two parts by this bisector line, and then the intensity profiles across each arm are scanned separately using the direction perpendicular to the arm axis found in step (iii). Gaussian fittings are used to obtain points on central axes of each arm. Similar to step (iii), these central points close to the arm tips and the CoB are eliminated, and the rest are linearly fitted to find the central axes of two arms.

With the central axes and the CoB position as inputs, we repeat step (iv). We find that single iteration is sufficient to achieve the optimized precision and that further iterations result in less than 10 nm variations in results. As shown in Figure 2.4.1(e), the coordinates of the CoB are used to represent the particle position, and the angle made by
Figure 2.4.1 Image processing steps: (a) an optical microscopic image of a boomerang particle with 110° apex angle; (b) inverted image of (a); (c) image after Gaussian filter smoothing and back ground subtraction. The green box indicates the area of interest; the yellow dashed lines indicate three parallel scanning lines in a scanning direction. (d) Central points of each arm determined from intensity profile scanning along different directions. The cross point between the central axis of each arm gives the center of the body (CoB). Yellow lines are schematic intensity scanning lines for step (iv) as described in the text. (e) Refined processing results of the central axes of the arms. ($x_1$-$x_2$): the lab frame coordinate system; ($X_1$-$X_2$) the body frame coordinate system. θ is the orientation of the particles. (f) An exemplary Gaussian fitting to a typical scanned intensity profile [65]. Copyright © 2013 American Chemical Society
the angle bisector with the horizontal axis defines the angular orientation of the boomerang. For the body frame coordinate system, the angle bisector of the arms is set as the $X_1$ axis, and the $X_2$ axis is defined based on $X_1$ [Figure 2.4.1(e)].

2.4.2 Trajectory Merging

As limited by the computer memory, each video taken with the EMCCD contains 3000 frames. Since a sufficient length of trajectories is essential to obtaining the mean displacements and displacement probability distribution functions with good averaging, we have taken 167 videos for a particle with 90° apex angle and 35 videos for each of two other particles. After all videos were image processed, the trajectories of the same particle were merged into a single long trajectory. To merge the trajectories of two videos together, the particle positions of the second video are shifted such that the position of the first frame in the second video matches that of the last frame in the first video. The trajectory of the second video then undergoes a rotation transformation to make the particle orientation of the first image match that of the last image in the first video. Random sequences of merging these trajectories provide additional averaging at long times. This video merging has enabled us to measure mean displacements and mean square displacements over 4 decades of time scales with excellent averaging [64].

The process of merging multiple videos of motion trajectories into a single trajectory is based on the assumption that the motions of the particle in the nearest neighboring time intervals are uncorrelated, an assumption which is physically justified. As shown by Alder and Wainwright and others [66-70], for a hard sphere suspended in fluid, the velocity correlation function decays algebraically with time with a power depending on
the dimensionality of the system. This so-called “long-time tail” originates from hydrodynamics, i.e. the diffusive transportation of momentum of the particle through the fluid. For a 1 μm diameter colloidal particle suspended in water, the decay time of the long-time tail is in the order of microseconds for water solvent. The time interval $\tau = 0.05$ s in our experiment is at least three orders of magnitude larger than the decay time of the hydrodynamic long-time tail, and therefore the correlations between the velocities or between the displacements in two neighboring time intervals are negligible. In experiments, we verified that the correlations between translational or angular displacements in next nearest time intervals are indeed zero within statistical errors.

### 2.4.3 Imaging and Tracking Precision and Accuracy

The precision in determining the particle’s position and orientation is limited by several physical factors, including intensity fluctuations of the illuminating light, mechanical vibrations of the microscope stage and electronic noises from the EMCCD detector. To determine the precision of our imaging and image processing system, a cell containing the boomerang particles was dried and then videos of an immobilized boomerang particle were taken for 150 seconds (3000 frames). The trajectory of this immobilized particle shows that the variations in the particle positions and orientations are approximately within 30 nm and 0.01 rad respectively [Figure 2.4.2(a-c)]. We calculated the variation probability distribution functions (PDFs) for both positions and orientation, and fitted these PDFs with Gaussian functions. The standard deviations of
Figure 2.4.2 (a-c) Position and orientation of an immobilized particle versus time. (d-f) Probability functions of the variations, $\Delta x_1$, $\Delta x_2$ and $\Delta \theta$ calculated from the trajectories in (a-c). Red lines represent best Gaussian fittings with the standard deviations $\sigma_{x_1} = 13$ nm, $\sigma_{x_2} = 11$ nm, and $\sigma_\theta = 0.0042$ rad [65]. Copyright © 2013 American Chemical Society
these Gaussian fittings, or the precision of our optical microscopy system and image processing algorithm is ±13 nm for particle position and ±0.004 radian for particle orientation.

To further illustrate the precision of our imaging and image processing system, we set the motorized stage of the optical microscope to move by ~100 nm in steps, and record a video of the immobilized particle. The image-processed positions of the particle as shown in Figure 2.4.3 demonstrate that the precision of our system does go far below 100 nm. Here the step size of the stage movement varies a little around 100 nm, which is ascribed to some hysteresis in the motorized stage.

Figure 2.4.3 Position of the immobilized particle versus time. The motorized microscope stage moves in the x-direction with ~100nm step size [65]. Copyright © 2013 American Chemical Society

To further illustrate the precision of our imaging and image processing system, we set the motorized stage of the optical microscope to move by ~100 nm in steps, and record a video of the immobilized particle. The image-processed positions of the particle as shown in Figure 2.4.3 demonstrate that the precision of our system does go far below 100 nm. Here the step size of the stage movement varies a little around 100 nm, which is ascribed to some hysteresis in the motorized stage.
To determine the accuracy of the image processing algorithm, we generated images with known particle positions and orientations with a computer program. We define the CoB and 9 additional equally spaced points on each boomerang arm, and then create a root image of the boomerang particle by summing point spread functions peaked at these points. By adding random Gaussian noises with set variance onto this root image, a sequence of images can be generated, mimicking the video of a fixed particle. Similar to the experiments, the mean background intensity is set at 0.32 (the maximum intensity is set as unity). To see the effect of particle orientations on image processing, we generated videos of boomerang particles with different set orientations. For each particle orientation, we created five videos corresponding to five different levels of Gaussian noises. The level of Gaussian noises is determined by the variance, \( \sigma_{\text{noise}}^2 \), of the background intensity. For convenience, we take the set CoB position as the origin and only present results for the \( x_1 \) position (results for \( x_2 \) are the similar).

We analyzed these simulated videos using our image processing algorithm, and observe that the mean positions \( \bar{x}_1 \) of the CoB deviate from the origin and vary with the set particle orientations [Figure 2.4.4 (a)]. This deviation results from the anisotropy of the pixel grids and decreases with the increase of the image magnification. The standard variations around the mean positions show little angle dependence and grow with the noise level. When the noise level is equivalent to that in the experiments (\( \sigma_{\text{noise}}^2 = 6.25 \times 10^{-10} \)), the standard variation around the mean position is around ±11nm, which is in good agreement with the experimental result ±13nm. As for the positional accuracy, we use the summation of the standard variations of the mean positions for different set orientations.
Figure 2.4.4 Results from computer-simulated images: (a-b) Mean position and orientation calculated from two set particle orientations (60° and 30°) versus the background noise. The error bars represent standard variations around the mean positions/angles. (c-d) Mean position and orientation averaged over different set orientations versus the background noise. The error bars represent the summation of the standard variations of the mean positions/angles from the set values at different set angles and the standard variations around the mean positions/angles [65]. Copyright © 2013 American Chemical Society
and the standard variations of the positions around the mean positions [Figure 2.4.4 (c)]. For noises equivalent to the experimental condition, the positional accuracy of our image processing algorithm is around ±32nm.

Similar analyses for the particle orientations are performed to estimate the angular accuracy. The deviations of the mean particle orientations from the set values are quite small (~0.001 rad) and independent of the set orientations [Figure 2.4.4 (b)]. As for the angular accuracy, we use the summation of the standard variations of the mean angles from the set values and the standard variations around the mean positions [Figure 2.4.4 (d)]. For noises equivalent to the experimental condition, the accuracy of our image processing algorithm is ~0.006 rad.

2.5 Summary

In this chapter, we presented the fabrication processes for making symmetric and asymmetric boomerang particles. The boomerang particles were fabricated using a photosensitive polymeric photoresist by projection lithographic technique. The photo-mask defined the size and apex angle of the fabricated boomerangs. As no software for tracking arbitrary shaped rigid bodies is commercially available, a high precision image processing algorithm for tracking the translational and rotational motions of boomerang shaped colloidal particles confined in quasi-2D geometries was developed.

By studying the displacement probability distribution of an immobilized particle, the precision of our imaging and image processing algorithm was shown to achieve 13 nm for position and 0.004 rad for orientation. Based on zero correlations between the displacements in neighboring time intervals, we merged trajectories of different videos of
the same particle into a long time trajectory, allowing for measurements of mean displacements, mean square displacements with excellent averaging. By using this image processing algorithm, we will study the local behaviors and measure the diffusion coefficients of boomerang particles in the following chapters.
CHAPTER 3

BROWNIAN MOTION OF SYMMETRIC BOOMERANGS

3.1 Introduction

In this chapter we study the Brownian motion of boomerang-shaped colloidal particles under quasi two-dimensional confinements. The boomerang particles with C\textsubscript{2v} mirror symmetry represent an attractive system for studying the Brownian motion of low symmetry particles because their CoM and CoH do not coincide and both lie outside the body. Especially, the location of the CoH is unknown before the motion of any tracking point (TP) is analyzed. Boomerang particles are also an interesting model system for active microswimmers [54], the electro-optical properties of DNA molecules [71-74] and the liquid crystal ordering [57].

The boomerang colloidal particles are fabricated from photo-curable polymer (SU8) by using photolithography [58] as described in Chapter 2. The particles used for our experiment have a 2.1 μm arm length, 0.51 μm thickness, 0.55 μm arm width and 90° apex angle [Figure 3.1.1(a)]. The aqueous suspension of the particles, stabilized by adding sodium dodecyl sulfate, (SDS, 1mM) was filled in a cell of ~ 2 μm thickness. Videos of isolated moving boomerangs were taken using a CCD camera at time step \( \tau = 0.05 \) s. Limited by the computer memory, each video contains 3000 frames and a total of 167 videos were taken for the same particle.

The image processing algorithm developed in chapter 2 was used to track the position and orientation of the boomerang particles. The cross-point between the central
Figure 3.1.1 (a) SEM image of the boomerang particles fabricated on silicon wafer. (b) Optical microscopic image and schematics of the coordinate systems. $(x_1-x_2)$: the lab frame and $(X_1-X_2)$: the body frame. (c) Representative trajectories of 5 different total lengths of time, where the red spots represent the positions of the CoH, and the boomerang is colored-coded in time. (d) An exemplary 300s trajectory for the CoH (green) and the CoB (blue) [64]. Copyright © 2013 American Physical Society
axes of the two arms represents the center of the body (CoB) and is a convenient point for motion tracking. The angle bisector gives the particle orientation $\theta$ [Figure 3.1.1(b)]. Trajectories obtained from all videos were merged into a single trajectory of $\sim 5 \times 10^5$ frames. Figure 3.1.1(c-d) show representative trajectories of the CoB and CoH at different time scales where the coupling between translational and rotational motions can be easily observed (the method to locate the CoH will be discussed later).

3.2 Lab Frame Measurements

3.2.1 Crossover between Short and Long Time Diffusion

In Figure 3.2.1(a), the angle averaged MSDs of the CoB along $x_1$ and $x_2$ are identical, implying that the Brownian motion is isotropic on average. In contrast the MSDs for ellipsoids that grow linearly with time, the MSDs for the boomerangs exhibit linearity with time only at short and long times with a nonlinear crossover region around $t = 10$ s. Best linear fittings give the short- and long-time diffusion coefficients respectively as $D^{ST} = 0.082 \, \mu\text{m}^2/\text{s}$, $D^{LT} = 0.057 \, \mu\text{m}^2/\text{s}$. In Figure 3.2.1(b), The rotational Brownian motion is linear for all times $\langle [\Delta \theta(t)]^2 \rangle = 2D_0t$, with the diffusion coefficient $D_0 = 0.044 \, \text{rad}^2/\text{s}$.

To discern anisotropic features in the Brownian motion, we measured the MSDs with the initial angle fixed at $\theta_0=0$. Due to its anisotropic shape, the MSDs at short times exhibit different diffusion coefficients along $x_1$ and $x_2$. At long times when the directional memory is washed out, the MSDs grow again linearly with $t$ with identical slope for both $x_1$ and $x_2$ [Figure 3.2.1 (c)]. To note, the MSDs along $x_1$ is larger than that along $x_2$ at long
Figure 3.2.1 (a) MSDs of the CoB in the lab frame vs. $t$. Red line: the best linear fit for $t < 10s$; dark brown line: theoretical fit using Eq. (3.9). Inset: linear plot of MSDs vs. $t$. (b) MSDs of $\theta$ vs. $t$ with the best linear fitting (red line). (c) MSDs for the CoB in the lab frame with $\theta_0 = 0$. Red lines: theory curves with Eq. (3.8). (d) MDs in the lab frame with $\theta_0 = 0$. Red line: theory curve of Eq. (3.7) using $D_\theta$ and $D_{\theta\theta}$ obtained from Figure 3.2.1 (b) and Figure 3.3.1 (e) [64]. Copyright © 2013 American Physical Society
times. As a comparison, MSDs for ellipsoids are identical along $x_1$ and $x_2$ at long times [6].

### 3.2.2 Non-Zero Mean Displacements (MD)

Although the MDs for Brownian motion are typically zero, we find that it is not the case for the boomerangs. The MDs averaged over different initial angle $\theta_0$ are indeed zero. However, with initial angle fixed at $\theta_0=0$, the MDs along $x_1$ are non-zero [Figure 3.2.1 (d)] and saturate at long times. Such non-zero MDs along the symmetric line are in sharp contrast with the zero MDs observed for spheres and ellipsoids.

### 3.2.3 Langevin Theory and Comparison with Experiments

To understand these observations, we assume that the boomerangs confined in 2D possess a CoH (as will later be proved experimentally). As pointed out by Brenner and others [23-28], the center of hydrodynamic stress (CoH) is located on particle’s symmetric lines. Assuming that the CoH for the boomerang is located at $(x_1^{CoH}, x_2^{CoH})$ on the bisector of the apex angle, then the position of a tracking point (TP) on the symmetry line is simply the sum of the CoH position vector and the vector $r = -r\cos \theta \hat{x}_1 - r\sin \theta \hat{x}_2$ from the CoH to the TP:

$$
\begin{pmatrix}
    x_1(t) \\
    x_2(t)
\end{pmatrix}
= \begin{pmatrix}
    x_1^{CoH}(t) \\
    x_2^{CoH}(t)
\end{pmatrix}
- r \begin{pmatrix}
    \cos \theta(t) \\
    \sin \theta(t)
\end{pmatrix}
$$

(3.1)

where $\theta(t)$ is the orientation of the particle. Therefore the motion of the TP can be described by:
Since the displacements of $x^{CoH}$ and $r$ are not correlated, i.e., $\langle [\Delta x_i^{CoH}(t)] [\Delta r_i(t)] \rangle = 0$, the mean displacements (MDs) and mean square displacements (MSDs) of the TP can be written as [see Appendix]:

$$\langle \Delta x_i(t) \rangle = \langle \Delta x_i^{CoH}(t) \rangle + \langle \Delta r_i(t) \rangle$$

$$\langle [\Delta x_i(t)]^2 \rangle = \langle [\Delta x_i^{CoH}(t)]^2 \rangle + \langle [\Delta r_i(t)]^2 \rangle$$

where $i = 1, 2$.

When the CoB is used as the TP, we denote the CoB-CoH separation as $d_0$. From the definition of the CoH, the descriptions of the Brownian motion of the CoH requires only one rotation diffusion coefficient $D_\theta$ and two translation diffusion coefficients $D_{22}^{CoH}$ and $D_{11}^{CoH}$, and therefore the Langevin equations for the CoH are actually the same as those for an ellipsoid and written as:

$$
\begin{pmatrix}
\dot{X}_1^{CoH} \\
\dot{X}_2^{CoH} \\
\dot{\theta}(t)
\end{pmatrix}
= 
\begin{pmatrix}
\xi^{CoH}_{11} & 0 & 0 \\
0 & \xi^{CoH}_{22} & 0 \\
0 & 0 & \xi^{\theta \theta}(t)
\end{pmatrix}
\begin{pmatrix}
X_1^{CoH}(t) \\
X_2^{CoH}(t) \\
\theta(t)
\end{pmatrix}
+ 
\begin{pmatrix}
\xi_1(t) \\
\xi_2(t) \\
\xi_\theta(t)
\end{pmatrix}
$$

(3.5)

where $\xi^{CoH}_{\theta \theta}$ is the hydrodynamic resistance tensor. The Gaussian random noise $\xi_i(t)$ is related to the resistance tensor through the fluctuation-dissipation theorem:
Here $i, j = 1, 2, \theta$. The calculations of MD and MSD for CoH and that for the vector $r$ are shown in the Appendix. Therefore using Eq. (3.3) and (3.4) the MDs and MSDs of the TP for fixed initial angle $\theta_0$ can be written as [75, see Appendix]:

$$\langle \Delta x_i(t) \rangle_{\theta_0} = r a_i \tau_i(t)$$

(3.7)

$$\left\langle \left[ \Delta x_i(t) \right]^2 \right\rangle_{\theta_0} = 2 \overline{D}_{CoH} t + \cos 2\theta_0 (r^2/2 + \Delta D/4D_\theta) b_i \tau_i(t) + 2r^2 a_i^2 \tau_1(t)$$

(3.8)

where $\tau_n = 1 - \exp(-nD_\theta t)$, \(a_1 = \cos \theta_0\), \(a_2 = \sin \theta_0\), \(b_1 = -1\), \(b_2 = 1\), \(\overline{D}_{CoH} = (D_{11}^{CoH} + D_{22}^{CoH})/2\), \(\Delta D = D_{22}^{CoH} - D_{11}^{CoH}\). Eq. (3.7) indicates that $\langle \Delta x_i(t) \rangle_{\theta_0}$ for the CoB saturates at $r = d_\theta$ in the long time, or the Brownian motion is biased towards the CoH. These theoretical expressions agree well with the experimental results [Figure 3.2.1 (c-d)].

Averaging Eq. (3.7) and (3.8) over different initial angle $\theta_0$ leads to that the angle averaged MDs are zero and the angle-averaged MSDs are expressed as [75, see Appendix]:

$$\left\langle \left[ \Delta x_{1,2}(t) \right]^2 \right\rangle = 2 \overline{D}_{CoH} t + r^2 \tau_1(t)$$

(3.9)

Here the crossover time of the $\tau_1(t)$ term is determined by the rotational diffusion coefficient, $\tau_\theta = 1/(2D_\theta) = 11$ s. Eq. (3.9) indicates that the short-time diffusion coefficient, \(\overline{D}^{ST} = \overline{D}_{CoH} + r^2D_\theta / 2\), is dependent on the position of the TP, while the
long time diffusion coefficient, $\overline{D}_{LT}^{\text{CoH}}$, is independent of the TP. This expression fits very well the experimental data [Figure 3.2.1(a)]. This crossover has been predicted by previous theory [27, 76] and is observed for the first time in experiments.

Our model also provides a clear physical picture of the nonzero MDs and the crossover between short- and long-time diffusion. As the rotational Brownian motion produces random displacements of the CoB on an arc with the CoH as its center, the projected displacements are symmetric to the CoB along the $X_2$ direction, while biased towards the arc center (i.e., the CoH) along the $X_1$ direction. When this Brownian orbital motion of the CoB covers a circle for $t > \tau_\theta$, the MDs saturate and the Brownian motion crosses over to the long-time diffusion.

### 3.3 Body Frame Measurements

To measure the other elements of the diffusion tensor, the translational displacements need to be transformed into a body frame co-moving with the particle. One convenient body frame has its origin fixed at the CoB and $X_1$ axis coincident with the symmetry axis [Figure 3.1.1(b)]. The displacements between consecutive body frames were obtained from those in the lab frame through the rotational transformation $\Delta X_i(\tau, t_n) = R_{ij}(\theta_n) \Delta x_j(\tau, t_n)$, where $i, j = 1$ or $2$, and $R_{ij}(\theta_n)$ is the rotation transformation matrix. The body frame trajectories are constructed by accumulating the displacements, $X_i(t_n) = \sum_{k=0}^{n} \Delta X_i(t_k)$. 
3.3.1 Distinction between Two Body Frames

One has two different choices of $\theta_n$: $\theta_n=\theta(t_n)$ representing the orientation at the beginning of each time interval, or $[\dot{\theta}(t_n)+\theta(t_{n+1})]/2$ representing the average orientation during the time interval. One previous work shows that these two choices give indistinguishable results for particles of high symmetry like ellipsoids [6]. However, we find that the distinction between these two frames becomes important for low-symmetry particles such as the boomerangs. We term the first $[\theta_n = \theta(t_n)]$ as the discrete body frame (DBF) and the second $[\theta_n = [\dot{\theta}(t_n)+\theta(t_{n+1})]/2]$ as the continuous body frame (CBF) [64].

In the CBF, the measured MDs along both $X_1$ and $X_2$ directions are zero [Figure 3.3.1 (a)], and the MSDs are linear with time, $\langle [\Delta X_i(t)]^2 \rangle = 2D_{ii} t$ with the diffusion coefficients $D_{11} = 0.049 \mu m^2/s$ and $D_{22} = 0.117 \mu m^2/s$ [Figure 3.3.1 (c)]. In contrast, very different behaviors are observed in the DBF. While the MD along $X_2$ is zero, the MD along $X_1$ is nonzero and grows linearly with time [Figure 3.3.1 (b)]. Accompanying this nonzero drift, the MSDs along $X_1$ exhibit nonlinearity with time [Figure 3.3.1 (d)]. Since the orientation of the DBF is reset at the beginning of each time step, the non-zero value of $\langle \Delta X_i \rangle$ seen in the DBF is actually a manifestation of the non-zero MDs $\langle \Delta x_i \rangle$ observed in the lab frame for $\theta_0=0$.

Since the displacements of the CoB along $X_2$ tend to induce rotation and vice versa, the coupled diffusion coefficient $D_{2\theta}$ is nonzero. While the translational motion of the CoB along $X_1$ is decoupled with rotation, $D_{1\theta}$ is thus zero. Our experimental results show that the DBF and CBF give rise to similar results for the translation-rotation correlation functions [Figure 3.3.1 (e, f)]. Linear fitting of these data with
Figure 3.3.1 (a-b) MDs vs. $t$ in the CBF (a) and DBF (b). The red line in (b) is the theory curve of Eq. (3.18). (c-d) MSDs vs. $t$ in the CBF (c) and DBF (d). In (c), the red lines are the best linear fittings. In (d), the dark brown curve is Eq. (3.19) with $D_\theta$ and $D_{2\theta}$ obtained from the data in Figure 3.2.1 and the red straight lines have same slopes as those in (c). (e-f) Translation-rotation correlations vs. $t$ in the CBF (e) and DBF (f). The red lines are the best linear fitting [64]. Copyright © 2013 American Physical Society
\( \langle \Delta X_i(t) \Delta \theta(t) \rangle = 2 D_{i \theta} \) gives a negligible value for \( D_{1 \theta} \leq -0.002 \text{ \mu m\cdot rad/s} \), and \( D_{2 \theta} = 0.051 \text{ \mu m\cdot rad/s} \) [Figure 3.3.1 (e, f)].

### 3.3.2 Langevin Theory in these Body Frames

Since the displacements obtained from the trajectories are in the lab frame, a rotation transformation needs to be performed to determine the elements of the diffusion tensor in the body frame. We start with velocities in the body frame which are related to those in the lab frame through the rotational transformation:

\[
\begin{align*}
\dot{X}_1(t) &= \cos \theta'(t) \dot{x}_1(t) + \sin \theta'(t) \dot{x}_2(t) \\
\dot{X}_2(t) &= -\sin \theta'(t) \dot{x}_1(t) + \cos \theta'(t) \dot{x}_2(t)
\end{align*}
\]  

(3.10)

where \( \theta'(t) \) is the angle used to transform the lab frame velocity (and displacements) into the body frame. To note, we use \( \theta'(t) \) to distinguish it from \( \theta(t) \). Using Eq. (3.2) yields (see Appendix):

\[
\begin{align*}
\dot{X}_1(t) &= \dot{X}_1^{CoH}(t) + \sin[\theta(t) - \theta'(t)] r \alpha_{\theta} \dot{\eta}_{\theta}(t) = \dot{X}_1^{CoH}(t) + \dot{R}_1(t) \\
\dot{X}_2(t) &= \dot{X}_2^{CoH}(t) - \cos[\theta(t) - \theta'(t)] r \alpha_{\theta} \dot{\eta}_{\theta}(t) = \dot{X}_2^{CoH}(t) + \dot{R}_2(t)
\end{align*}
\]  

(3.11)

where \( \dot{R}_1(t) \) and \( \dot{R}_2(t) \) are the velocities of the vector \( r \) transformed into the body frame, and \( \dot{\theta}(t) = \sqrt{2D_\theta \eta_{\theta}(t)} = \alpha_{\theta} \dot{\eta}_{\theta}(t) \) (see Appendix). The MDs, MSDs and cross coupling of the TP in the body frame are simply (see Appendix):
In experiments, for the time interval between $t_n$ and $t_{n+1}$, one can choose either

\[
\theta(t) = \left[ \theta(t_n) + \theta(t_{n+1}) \right] / 2 ,
\]

which define a body frame noted here as the continuous body frame (CBF), or \( \theta(t) = \theta(t_n) \), which define another body frame noted here as the discrete body frame (DBF). As shown in Ref. [6], these two body frames yield the same results for ellipsoidal particles. Since the motion of CoH is the same as that for ellipsoids [75, see Appendix], we have \( \langle \Delta X_i^{CoH}(t) \rangle = 0 \) and \( \langle [\Delta X_i^{CoH}(t)]^2 \rangle = 2D_{ii}^{CoH} t \) where \( i = 1, 2 \).

There is also no coupling with the rotational diffusion at CoH and hence \( \langle \Delta X_i^{CoH}(t) \Delta \theta(t) \rangle = 0 \).

The differences between the CBF and DBF can be ascribed to the differences between the displacements of the vector \( r \) in these two body frames. Using Eq. (3.12), Eq. (3.13) and Eq. (3.14) the first and second moments of displacements for the TP can be expressed in the CBF as [75, see Appendix]:

\[
\langle \Delta X_1(t) \rangle = \langle \Delta X_2(t) \rangle = 0 \tag{3.15}
\]

\[
\langle \Delta X_1^2(t) \rangle = 2D_1 t = 2D_{11}^{CoH} t \tag{3.16}
\]

\[
\langle \Delta X_2^2(t) \rangle = 2D_2 t = 2\left(D_{22}^{CoH} + r^2 D_0 \right) \tag{3.17}
\]

and in the DBF as:
\[ \langle \Delta X_1(t) \rangle = rD_\theta t; \quad \langle \Delta X_2(t) \rangle = 0 \]  \hspace{1cm} (3.18)

\[ \langle \Delta X_1^2(t) \rangle = 2D_{11}^{\text{CoH}} t + (rD_\theta)^2 t^2 \]  \hspace{1cm} (3.19)

\[ \langle \Delta X_2^2(t) \rangle = 2D_{22} t = 2\left(D_{22}^{\text{CoH}} + r^2 D_\theta\right) \]  \hspace{1cm} (3.20)

The CBF and DBF give the same forms for the translation-rotation correlation functions:

\[ \langle \Delta X_1 \Delta \theta \rangle = 0, \quad \text{and} \quad \langle \Delta X_2 \Delta \theta \rangle = 2D_{22} t = 2rD_\theta t \]  \hspace{1cm} [75, see Appendix].

Based on Eq. (3.7) and Eq. (3.18), the slopes of the MDs vs. time are the same at short times in the DBF and in the lab frame (for \( \theta_0 = 0 \)), which agrees with the experiments [Figure 3.1.1 (d), Figure 3.3.1 (b)]. Employing the DBF provides a physical picture consistent with the lab frame observations, while using the CBF averages out the drift term in MDs and the nonlinear components in MSDs and provides a convenient way to calculate diffusion coefficients.

### 3.4 Determination of the Center of Hydrodynamics (CoH)

#### 3.4.1 Diffusion Coefficients vs. Tracking Point

To verify the existence of the CoH, we re-calculated the trajectories and the diffusion coefficients for TPs on the symmetry line which have different distance \( d \) from the CoB, here \( d = d_0 - r \). \( D_{22} \) and \( D_{2\theta} \) can be derived from the above equations as a function of \( r \): \( D_{22} = D_{22}^{\text{CoH}} + r^2 D_\theta \), and \( D_{2\theta} = rD_\theta \). We see that the theoretical curves fit the experimental results well [Figure 3.4.1 (a, b)]: \( D_{11} \) remains unchanged, \( D_{22} \) reaches a minimum at \( d = 1.16 \mu m \) and \( D_{2\theta} \) increases with \( d \) and crosses zero approximately at
Figure 3.4.1 (a) $D_{11}$ and $D_{22}$ vs. $d$. Red and green lines are theory curves based on Eq. (3.16) and (3.17). (b) $D_{1θ}$ and $D_{2θ}$ vs. $d$. Red and green lines are the theory curves of $D_{2θ} = r D_θ$ and $D_{1θ} = 0$ respectively. The dashed lines indicate the CoH at $d_0 = 1.16$ μm [64].

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1.16 \mu m. These indicate that the CoH is at a distance $d_0 = 1.16 \mu m$ from the CoB, which agrees with $d_0 = D_{20}/D_0$.

### 3.4.2 Diffusion of the CoH

With the CoH as TP, the MSDs in the lab and body frames all grow linearly with time and the translation-rotation correlation functions are zero [Figure 3.4.2 (a-c)]. As expected, the differences between DBF and CBF disappear. The averaged diffusion coefficient for the CoH in the lab frame, $\bar{D}^{CoH} = 0.054 \mu m^2/s$, agrees with the long-time averaged diffusion coefficient of the CoB.

It is not trivial to validate the existence of the CoH for the boomerangs in quasi-2D confinements since previous theory shows that the Brownian motion of bent-rods in three dimensions exhibit screw-like properties [27]. Experiments with 1.7 \mu m and 1.9 \mu m thick cells for the same or different boomerang particles show qualitatively similar results with different values of diffusion coefficients. Cell confinements are known to significantly affect the diffusion coefficients [77-79]. It is worth to further explore in the future how the Brownian motion of the boomerangs crosses over from the non-skewed 2D behaviors to skewed 3D behaviors when the cell thickness is raised.

### 3.5 Dependence of Diffusion Coefficient on Apex Angles

We have seen above that when the CoB is used as the tracking point, translational motion along $X_2$ axis leads to particle rotation with respect to the CoB because of non-zero drag torque. Therefore, the coupled diffusion coefficient $D_{20}$ is non-zero, characterizing the coupling between rotation and translation along $X_2$ axis. The diffusion
Figure 3.4.2 (a) Angle averaged MSDs for the CoH measured in the lab frame. The red line is the best linear fit with $\bar{D}^{\text{CoH}}=0.054\mu\text{m}^2/\text{s}$. (b) MSDs of the CoH in the DBF. Red lines represent the best linear fitting with $D_{11}^{\text{CoH}}=0.049\mu\text{m}^2/\text{s}$ and $D_{22}^{\text{CoH}}=0.060\mu\text{m}^2/\text{s}$. For clarity, MSDs for $X_2$ are shifted by a factor of 2. (c) Translational and rotational displacement correlation functions calculated at CoH [64]. Copyright © 2013 American Physical Society
coefficient matrix of the boomerang particles in the body frame in two dimensions is given by

\[
D = \begin{pmatrix}
D_{11} & 0 & 0 \\
0 & D_{22} & D_{2\theta} \\
0 & D_{2\theta} & D_{2\theta}
\end{pmatrix}
\]  

(3.21)

After the image processing, we obtain the positions of the CoB, \(x(t_n) = [x_1(t_n), x_2(t_n)]\) and the orientation \(\theta(t_n)\) of the boomerang as functions of the instantaneous time \(t_n=nt\). The translational displacements in the lab frame are calculated as \(\Delta x_i(t_n)=x_i(t_n+t)-x_i(t_n)\), where \(i=1, 2\). The lab frame displacements need to be transformed into those in the body frame through a rotation transformation as before: \(\Delta X_i(t_n)=R(\theta_n)\Delta x_i(t_n)\), where

\[
R(\theta_n) = \begin{pmatrix}
\cos \theta_n & \sin \theta_n \\
-\sin \theta_n & \cos \theta_n
\end{pmatrix}
\]

For boomerangs, \(\theta_n\) needs to be chosen carefully since the Brownian motion is biased towards the CoH due to translation-rotation coupling, which may lead to non-zero drift and nonlinear MSDs in the body frame [64]. To eliminate the nonlinear behaviors as seen in section 3.3.1 we will limit all our calculations to continuous body frame defined by \(\theta_n = [\theta(t_n)+\theta(t_n+1)]/2\). As before the body frame trajectories are constructed by accumulating the displacements, \(X_i(t_n) = \sum_{k=0}^{n} \Delta X_i(t_k)\).

The diffusion coefficients are obtained from the displacements in the body frame through where \(i=1, 2, \theta\). The measured mean square displacements (MSDs) and translation-rotation displacement correlations for the CoB are shown in Figure 3.5.1 for the three different apex angles of the boomerang particles. The MSDs grow linearly with time; linear fittings yield the diffusion coefficients \(D_{11}, D_{22}\) and \(D_\theta\) [Figure 3.5.1(a-b)]. Due to the particle symmetry, displacements of the CoB along the \(X_1\) axis do not induce
rotations as the drag torques on the two arms cancel out. The experimental data verify that the correlations between displacements in $X_1$ and $\theta$ are zero (Figure 3.5.1(d)). In contrast, displacements of the CoB along the $X_2$ cause rotation as the drag torques of two arms add up. The experimental data show that the correlations between displacements along $X_2$ and $\theta$ grow linearly with time, and best linear fitting gives the coupled diffusion coefficient $D_{2\theta}$ for the three particles.

Figure 3.5.1(f) shows the variation of the measured diffusion coefficients for the CoB and also for CoH on the apex angle of the boomerangs. For the CoB, the translational, rotational and coupled diffusion coefficients show the same trend: decreasing with the increase of the apex angle. This result can be understood qualitatively. When the apex angle is increased, the effective cross-section of the particle along $X_1$ increases, or $D_{11}$ should decrease. Similarly, $D_\theta$ should decrease as the effective particle length is increased. Considering that the translation-rotation coupling is zero for $0^\circ$ and $180^\circ$ apex angles, the coupled diffusion coefficient $D_{2\theta}$ should be maximized at some angle between $0^\circ$ and $180^\circ$. This is qualitatively in agreement with theoretical calculations for bent-rods in three-dimensions [27].

In section 3.3.2 and 3.4.1, we have demonstrated that the diffusion coefficients $D_{22}$ and $D_{2\theta}$ are affected by the position of the tracking point used in the measurements [64]. For tracking points on the angle bisector line, $D_{11}$ and $D_\theta$ remain the same while $D_{22}$ and $D_{2\theta}$ vary with the position of the tracking point. The boomerang particle confined in
Figure 3.5.1 Measured mean square displacements for the CoB: (a) MSDs along $X_1$ versus time; (b) MSDs along $X_2$ versus time; (c) MSDs for $\theta$ versus time; (d) Correlation function between displacements along $X_1$ and $\theta$; (e) Correlation function between displacements along $X_2$ and $\theta$. The types of data points represent different particle apex angles: square ($\square$) for 90º, circle ($\circ$) for 110º and triangle ($\triangle$) for 120º. (f) Measured diffusion coefficients ($D_{11}$, $D_{22}$, $D_\theta$ and $D_{2\theta}$) for CoB (circles, $\circ$) and (square, $\square$) for the CoH as a function of the vertex angle of the boomerang particles. The unit of the vertical axis is $\mu m^2/s$ for $D_{11}$, $D_{22}$, $D_{2\theta}$, rad$^2$/s for $D_\theta$, and $\mu m\cdot$rad/s for $D_{2\theta}$ [65]. Inset shows the position of the CoH for the boomerangs with three different apex angles. Copyright © 2013 American Chemical Society
quasi-2D geometry possesses a CoH which is located on the symmetry line and at a distance \( d = D_{2\theta}/D_\theta \) from the CoB. As discussed above, \( D_\theta \) decreases with the increase of the apex angle as the effective particle length is increased. Hence the distance \( d \) of the CoH from CoB depends on that of \( D_{2\theta} \) which is maximized at some angle between 0° and 180°. At this CoH, the coupled diffusion coefficient \( D_{2\theta} \) becomes zero, the diffusion coefficient tensor is diagonal and \( D_{22} \) is minimal and given by \( D_{22}^{CoH} = D_{22} - D_{20}^2/D_\theta \) as seen in section 3.2.3 [64]. To exclude this dependence on tracking point, we re-calculated \( D_{22} \) at the CoH for these three particles. In comparison with \( D_{22} \), exhibits smaller \( \theta \) dependence [Figure 3.5.1(f)], and seems to flatten out when the apex angle is above 110°.

Intuitively, the cross-section area along \( X_2 \) axis is maximal for 0° and 180° apex angles, so is the Stokes drag force. Therefore, \( D_{22}^{CoH} \) should decrease when the apex angle approaches 0° and 180°, and the measured angle dependence of measured \( D_{22}^{CoH} \) is in qualitative agreement with this picture [65].

3.6 Summary

Our experimental and theoretical studies show that the diffusion of the boomerangs is rather different from that of spheres and ellipsoids. (1) The mean displacements (MD) for fixed initial angle are biased towards the CoH, and the mean square displacements (MSDs) exhibit a crossover from short to long time diffusion with different diffusion coefficients. (2) The boomerangs confined in quasi-two dimensions are non-skewed and possess a CoH where translation and rotation are decoupled in the body frame. (3) Our model based on Langevin theory shows that the non-zero MDs result
from the Brownian orbital motion of the TP with respect to the CoH. (4) Two methods for calculating body frame displacements which give indistinguishable results for ellipsoids [6], yield drastically different results for boomerang particles. Lastly, we measured the diffusion coefficients of boomerang particles of three different apex angles, the angle dependences of these diffusion coefficients agree qualitatively with expectations.
CHAPTER 4
NON-GAUSSIAN DISPLACEMENT PROBABILITY DISTRIBUTION FUNCTIONS

4.1 Introduction

The essence of Brownian motion is the random displacements of mesoscopic particles under the stochastic impacts of surrounding molecules. The probability distribution for the random displacements of spherical particles has been shown to be Gaussian by Einstein and others [1-3, 80, 81]. Recent studies, however, have shown that non-Gaussian displacement probability distributions are more common than expected in soft matter systems [6, 8, 82-86] owing to multiplicative noises of different physical origins. The experimental and theoretical studies by Han et al on Brownian motion of ellipsoidal particles show that the coupling of translational and rotational motion makes the random displacements in the lab frame non-Gaussian in small time scales [6]. Single particle experiments by Wang et al reveal that the Brownian motion of spherical particles may remain Fickian (i.e., the mean-square-displacement grows linearly with time) while exhibit displacement probability distribution functions with non-Gaussian tails when the particles are coupled with inhomogeneous environments such as phospholipid tubes and entangled f-actin networks [8].

In chapter 3 we have shown that the Brownian motion of boomerang shaped colloidal particles is remarkably different from that of spheres and ellipsoids [64]. For boomerangs, the mean square displacements are only linear at short and long times and the nonlinear during the cross-over. For fixed initial particle orientation, the mean
Figure 4.1.1 Optical microscopic picture of a boomerang colloidal particle confined in quasi-two dimensions. ($x_1$-$x_2$): the lab frame and ($X_1$-$X_2$): the body frame. The angle $\theta$ made by the symmetry axis $X_1$ with the $x_1$ axis in the lab frame gives the orientation of the particle at one instant of time. The center of hydrodynamics (CoH), the center of the body (CoB) and the point P located on the symmetry axis $X_1$ is used as tracking points.
displacements are biased towards the center of hydrodynamic stress (CoH). Our model based on Langevin theory indicates that these behaviors originate from translation rotation coupling which leads to the orbital motion of the tracking point with regard to the CoH. In this chapter we investigate how the translation rotation coupling depends on the tracking point and its effects on the displacement probability distribution function of the boomerang particles.

### 4.2 Experiments and Results

As described in chapter 2 the boomerang particles used in our study were made of photo-curable polymer SU8 by projection photolithography, and have 2.1μm arm length, 0.51μm×0.55μm arm cross-section and 90° apex angle [58, 65]. Aqueous suspensions of these boomerang particles are stabilized by 1mM sodium dodecyl sulfate (SDS). Cells made of glass slides with ~ 2 μm thicknesses were used to confine the colloidal particles in a quasi-two dimensional geometry. Particle concentrations were kept very low so that there are no hydrodynamic interactions between particles.

Brownian motion of the boomerangs was observed and recorded with an inverted optical microscope coupled with a digital CCD camera. Each video contains 3000 frames with 0.05 seconds time interval (τ). A total of 167 videos of the same boomerang particle were recorded and analyzed by using our high accuracy image processing algorithm developed in chapter 2. Similar to chapter 3 we will first track the cross point of the central axes of two arms of the boomerang which is the center of the body (CoB). The bisector of the apex angle was used to represents the particle orientation (Figure 4.1.1).
These trajectories were then merged in 24 different random sequences into a long trajectory, as discussed in chapter 2, totaling about 12 million frames [65].

Firstly we summarize our findings in chapter 3 on the Brownian motion of the boomerangs of the same size [64]. The rotational Brownian motion is diffusive at all times with a diffusion coefficient $D_\theta = 0.045 \text{ rad}^2/\text{s}$. The MSDs of the CoB in the body frame are linear with diffusion coefficients $D_{11} = 0.049 \mu\text{m}^2/\text{s}$ and $D_{22} = 0.117 \mu\text{m}^2/\text{s}$. Due to the $C_{2V}$ symmetry of the particles, there exists a coupled diffusion coefficient $D_{2\theta}$, which is measured to be $D_{2\theta} = -0.051 \mu\text{m}.\text{rad}/\text{s}$. Based on these diffusion coefficients, the center of hydrodynamic stress (CoH) is determined, at a distance $d_0 = D_{2\theta}/D_\theta$ from the CoB. At the CoH, both the coupled diffusion coefficients ($D_{1\theta}$, $D_{2\theta}$) are zero, $D_{11}$ remains the same as that measured at the CoB, and $D_{22}$ reaches its minimum, $D_{22} = 0.060 \mu\text{m}^2/\text{s}$.

Based on the relation $D_{2\theta} = rD_\theta$, we can study Brownian motion of the same particle with different levels of translation-rotation coupling ($D_{2\theta}$) by choosing different tracking points on the symmetry axis $X_1$. For the CoH, the translation-rotation coupling is zero in the body frame, $D_{2\theta}/D_\theta = 0 \mu\text{m}$. While for the CoB which is at a distance of $d_0$ from CoH, $D_{2\theta}/D_\theta = 1.16 \mu\text{m}$. We choose the third point P at a distance $r=5d_0$ from the CoH, where $D_{2\theta}$ is five times of that at CoB [Figure 4.1.1]. The trajectories for the CoH and P are obtained from the trajectory of the CoB by simply shifting the CoB position by a vector of $(-d_0\cos\theta, -d_0\sin\theta)$ and $(-5d_0\cos\theta, -5d_0\sin\theta)$ respectively.

The MSDs calculated for these three tracking points are shown in Figure 4.2.1. At the CoH, the MSDs grow linearly with time over the full range of observation time,
Figure 4.2.1 (a) Measured MSDs for the CoH, CoB and for the point P as the tracking point. Red lines are the theoretical curves using Eq. (4.1) and $D_\theta=0.044\text{rad}^2/\text{s}$, and $D_{\text{CoH}}=0.058\mu\text{m}^2/\text{s}$. (b) Data in (a) is re-plotted in logarithmic scale for clear display of the crossovers from short time faster to long time slower diffusion. The green dashed lines in (b) have the slopes equal to their short time diffusion coefficient.
similar to that of ellipsoids. For the CoB and P, the MSDs grow linearly with time at short and long times, while in the intermediate crossover regime the diffusion is sub-diffusive (non-Fickian). It can also be seen that the diffusion coefficients of CoB and P at long times are the same as the diffusion coefficient of the CoH. This crossover behavior has been predicted by Wegener [27], and is observed in experiments for the first time.

We have shown that the MSD of a point on the symmetry axis at a distance \( r \) from CoH as a function of time is given by [64, see Appendix]:

\[
\langle [\Delta x_{1,2}(t)]^2 \rangle = 2D_{CoH}t + r^2 \tau(t)
\]

(4.1)

where \( D_{CoH} = \frac{D_{11}^{CoH} + D_{22}^{CoH}}{2} \) is the average diffusion coefficient at CoH. \( D_{11}^{CoH} \) and \( D_{22}^{CoH} \) are the body frame diffusion coefficient at the CoH along the \( X_1 \) and \( X_2 \) direction. Using the measured diffusion coefficients, we see that Eq. (4.1) agrees excellently with the experimental data [Figure 4.2.1]. The characteristic crossover time can thus be determined as \( \tau_\theta \sim 1/2D_\theta \sim 10s \). Since the second term of Eq. (4.1) is proportional to \( r^2 \), the crossover behavior for P is more distinguishable than that for the CoB.

The measured probability distribution functions (PDFs) \( p(x, t) \) for displacements in the lab frame are plotted as functions of displacements along \( x_1 \) in Figure 4.2.2 for the three time regimes. Distributions along \( x_2 \) are similar. To facilitate comparisons with the Gaussian distribution, we scaled the vertical axis as \( p(x, t)\sqrt{t} \) and the horizontal axis as \( x/\sqrt{t} \). For the CoH [Figure 4.2.2(a-c)], the scaling plots collapse all the \( p(x, t) \) data into master curves for all three time regimes, while a comparison with the Gaussian function clearly shows that the PDFs deviate from Gaussian in both short [Figure 4.2.2(a)] and
intermediate time regimes [Figure 4.2.2(b)], while agree with Gaussian well in the long time regime [Figure 4.2.2(c)]. This non-Gaussian behavior originates from the difference between $D_{11}$ and $D_{22}$, the same as the Brownian motion of an ellipsoid [6]. While previous studies indicate that the short time PDFs for the ellipsoidal particles are quite complex [6], we found that the PDFs at short times can be well fitted with an empirical formula (red curve in Figure 4.2.2):

$$y = C_1 \left[ I - \exp(-C_2 x^2) \right] \exp\left(-C_3 x^2 \right)/x^2$$  \hspace{1cm} (4.2)

$C_1$, $C_2$ and $C_3$ are fitting parameters.

As for the CoB [Figure 4.2.2(d-f)], the scaling plots collapse the PDF data in short [Figure 4.2.2(d)] and long time regimes [Figure 4.2.2(f)], while the PDFs in the crossover regimes do not follow the scaling [Figure 4.2.2(e)]. In comparison with CoH, the deviation of the PDFs from the Gaussian distribution in the short time regime is increased. In particular, the probability of large displacements is increased, while the probability of small displacements still obeys approximately the Gaussian distribution with the short time diffusion coefficient $\overline{D}_{\text{CoB}}^{\text{ST}} = 0.082 \mu m^2/s$. Again, we found the PDFs can be well fitted with the same formula as for the CoH:

$$y = C_1 \left[ I - \exp(-C_2 x^2) \right] \exp\left(-C_3 x^2 \right)/x^2$$  \hspace{1cm} (4.3)

where $C_1$, $C_2$ and $C_3$ are fitting parameters. At the intermediate times only the central part of the PDF follows the master curve and the large displacement tails clearly are not scalable. Comparison with the Gaussian distribution with short time diffusion coefficient
Figure. 4.2.2 Scaling plots of measured displacement probability distribution functions for the CoH (a-c), the CoB (d-f) and the point P (g-i) along the $x_1$ axis in the short (a, d, g), intermediate (b, e, h) and long time (c, f, i) regimes respectively. Magenta curves in (a, b, c) represents Gaussian functions with CoH diffusion coefficient $\bar{D}_{\text{CoH}} = 0.058 \mu m^2/s$. For CoB in (d, e) magenta curves corresponds to Gaussian function with short-time diffusion coefficient $\bar{D}_{\text{CoB}}^{ST} = 0.082 \mu m^2/s$. Magenta curve in (f) corresponds to Gaussian function with long-time diffusion coefficient of CoB $\bar{D}_{\text{CoB}}^{LT} = 0.058 \mu m^2/s$. For P, magenta curve in (g) is the Gaussian function matching the central part of the scaled distribution. Gaussian function with short-time diffusion coefficient of P $\bar{D}_P^{ST} = 1.15 \mu m^2/s$ is shown in dashed brown. Magenta curve in (i) corresponds to Gaussian function with long time diffusion coefficient $\bar{D}_P^{LT} = 0.058 \mu m^2/s$ for P. The red curves in (a, d, g) represent empirical fitting.
specify variable diffusion coefficient at these time scales corresponding to the sub-diﬀusive regimes where the linear behavior of the MSD breaks down. The PDFs in the intermediate time regime evolve eventually to Gaussian form as the MSD reverts back to Fickian at long time. For the scaling, since the MSDs in Eq. (4.1) have a constant term \( r^2 \) at long time, we multiplied the long time PDFs and normalized \( x \) by \( \left( t + \frac{r^2}{2D_{CoB}^{LT}} \right)^{0.5} \), and could scale all data to a Gaussian curve with a variance corresponding to the long time diffusion coefficient \( D_{CoB}^{LT} = 0.058 \mu m^2 / s \).

The effects of translation-rotation coupling on the displacement probability distribution are made conspicuous for the tracking point P. As seen from the Figure 4.2.2(g-i), similar scaling is still applicable for the short and long time PDFs, indicating constant diffusion coefficients therein. However, the scaled short time PDFs deviates more from Gaussian [Figure 4.2.2(g)]; a comparison with the Gaussian distribution (dotted curve) corresponding to the short time diffusion coefficient shows that the behavior is distinctively different from that of the CoB distribution and variance of the central part that fits with Gaussian (pink curve) is much smaller than that obtained from the short time diffusion coefficient. The contribution to the PDF is predominantly from the large displacement steps which noticeably belong to a non-Gaussian distribution. We also found that the scaled short-time PDFs can be well fitted with a similar formula but with a different exponent:
where $C_1, C_2$ and $C_3$ are fitting parameters. Similarly, the PDFs for the intermediate time [Figure 4.2.2(h)] range do not follow the scaling behavior with increased discrepancies, and the long-time scaling of PDFs of the point P shows a Gaussian distribution [Figure 4.2.2 (i)].

The motion of the point P clearly revealed the fundamental difference, particularly at short times, in the distribution when the tracking point is not coincident with CoH. The short time diffusion underlines the local behavior of the particle. At long time the distribution evolves to Gaussian dictated by the central limit theorem. For ellipsoids the diffusion is faster along its long axis than in the traverse direction at short time [6]. However this tendency is opposed by rotational diffusion and the motion becomes isotropic at long time. For the boomerangs, the $X_2$ direction [Figure 4.1.1] corresponds to the long axis but as a consequence of CoH not coincident with CoB the translational motion along $X_2$ leads to a rotation and the boomerang travels in a circular path about the CoH as discussed in chapter 3. For the short axis that is the $X_1$ direction there is no coupling with rotation similar to an ellipsoid. Thus the short time behavior of the boomerangs is inherently different from the ellipsoids whose distribution is similar to that of the CoH where the translation-rotation is decoupled in the body frame.

For anisotropic particles the statistics of the short time local behaviors are best observed if the initial lab frame orientations are fixed and the particles are allowed to
Figure 4.2.3 Two dimensional displacement probability distribution for the CoH (a-d), the CoB (e-h) and for the point P (i-l) at different times for the initial $\theta_0=0$. The abscissa corresponds to the $x_1$ direction and the ordinate $x_2$ direction. For the CoB and P, the position of the CoH is shown by the dot in (e-l). Red corresponds to maximum probability and blue corresponds to zero probability of finding the particle.
diffuse. At short time the behaviors in the lab with fixed initial orientation of the particles are similar to the displacements in the body frame along the body frame axes. For random initial orientations these fundamental details of the particle motion are averaged out before the characteristic rotational time $\tau_\theta$. In Figure 4.2.3 we plot the 2D probability distribution of CoH, CoB and the point P for the boomerang in lab with fixed initial orientation $\theta=0$ for which the symmetry axis $X_1$ is parallel to the $x_1$ direction. It is assumed that each of these tracking points is at the origin at time $t=0$ and the distribution is allowed to evolve in time. For the motion of the CoB and the point P the position of CoH at time $t=0$ is marked on the $x_1$ axis as shown in Figure 4.2.3.

The CoH motion similar to that of an ellipsoid is quasi-Gaussian and anisotropic at short times and crosses over to long time Gaussian distribution [Figure 4.2.3(a-d)]. At short time the distribution is anisotropic [Figure 4.2.3(a)] as the point diffuses more along the $x_2$ direction, which represents the long axis for fixed initial orientation. However this is not that obvious here due to the small difference in mobility along $X_1$ and $X_2$ axis at the CoH.

For the CoB [Figure 4.2.3(e-h)] and the point P [Figure 4.2.3(i-l)] distribution, as the tracking point moves away from the CoH the diffusion coefficient along $X_2$ not only increases but also gets coupled with rotation. In contrast that along $X_1$ remains the same as that of the CoH and is decoupled from rotation. This behavior gives rise to the radial mode of the diffusion of the tracking point about the CoH. The motion can be visualized as the superposition of the motion of the CoH and the orbital motion of a vector $r$ from the CoH to the tracking point as observed in chapter 3. If the diffusion along $x_1$ is small,
the radial mode of diffusion of the tracking point is similar to the diffusion of the particle in a ring-shaped channel with a given initial position. Therefore as the probability distribution for the particle spreads around the channel the average position of the particle asymptotically approaches the CoH. The effects are less prominent in the CoB distribution which is at a distance $d_0=1.16 \ \mu m$ from the CoH. Figure 4.2.3(e-h) shows that the distribution shifts towards the CoH with time and at $\sim 100s$ it is at CoH [Figure 4.2.3(g)] and finally evolves to a Gaussian distribution at very long time.

The orbital mode of diffusion at short times is distinctively prominent in the motion of the point P which is at a distance $r=5d_0$ and therefore the translation-rotation coupling is fivefold stronger than that at CoB. The distribution is non-Gaussian and uniquely different from that of the CoH. In the intermediate time the distribution evolves through a half moon and donut shape centering the CoH at 10 sec and 100 sec respectively [Figure 4.2.3(j-k)]. At long time, as a consequence of the central limit theorem all distributions are Gaussian and similar to CoH motion. The tracking point and shape of the particle is irrelevant at these time scales.

4.3 Summary

In conclusion, using single particle tracking we have shown that the distribution of displacement probability of Brownian boomerangs is non-Gaussian at short time although the MSDs grow linearly with time. At long time distribution becomes Gaussian; however in the intermediate time the MSDs are sub diffusive. The displacements probability functions collapse to a master curve at long and short times and they are non-scalable in the intermediate time regime. This behavior arises from the fact
that the CoB of the boomerangs is not coincident with that of the CoH leading to translation rotation coupling. We confirm this phenomenon by calculating the displacement distribution function at a point P far away from the CoH where the translation–rotation coupling is enhanced. Interestingly the tails of the displacement probability functions calculated for the point P are in close resemblance with the distributions of colloidal beads tethered on phospholipids bilayer or entangled actin filaments as shown by Wang et al [8]. This implies that such behaviors in these systems arise from strong translation rotational coupling. Moreover, boomerangs represents the class of rigid bodies of more general shapes with reduced symmetry similar to biological macromolecules and particles encountered in nature are of highly anisotropic shapes. Therefore our results raise fundamental questions about the underlying statistical nature of their distribution function which is only Gaussian for spherical particles.
CHAPTER 5

BROWNIAN MOTION OF ASYMMETRIC BOOMERANGS

5.1 Introduction

In this chapter we extend our work on Brownian motion for the case of asymmetric boomerangs with two unequal arms and study their motion in a quasi-two dimensional geometry. Asymmetric boomerangs with no plane of symmetry in two dimensions represent the class of rigid bodies of most general shape. Our study show that CoH exists even for the asymmetric boomerangs in two dimensions. This suggests that the behavior is more generic and for non-chiral objects it is always possible to find the CoH and that the translation-rotation motion in two dimensions can be decoupled at this point.

We use a projection lithography system to fabricate the asymmetric boomerang particles [58, 65] as described in Chapter 2. The photomask defined the shape of the particles on the UV curable photoresist SU8. Boomerang particles with unequal arm lengths of different sizes and apex angles were fabricated. The particle used for this study has a long arm length of 2.25 μm and the short arm length is 1.3 μm with 90° apex angle [Figure 5.1.1(b)]. The arm width of the particle is 0.7 μm and the thickness ~ 0.51 μm defined by the thickness of the photoresist layer. Surfactant SDS (1mM) was used to stabilize the aqueous suspension of the particles. Cells of ~ 1.7 μm thickness made of parallel glass slides with spacers were fabricated to restrict the motion of the particles in two dimensions. Videos of individual isolated asymmetric boomerangs were recorded at
Figure 5.1.1 (a) Diffusion coefficients of particles in two dimensions with different numbers of symmetry planes. (b) SEM image of the asymmetric boomerang particles fabricated on silicon wafer with 90° apex angle. (c) Schematics of the coordinate systems ($x_1$-$x_2$): the lab frame and ($X_1$-$X_2$): the body frame. The CoH and the CoM are shown in red and green respectively. $\vec{r} = \vec{r}_1 + \vec{r}_2$ is the vector from the CoH to the tracking point. Inset shows a image processed optical microscopic image.
time step $\tau = 0.05$ s with a CCD. We are limited to 3000 frames for each video by the memory of the computer. 200 videos for the same particle at similar time steps were recorded.

We implement our algorithm developed [65] in Chapter 2 to image process each video frame extracted from the recorded videos. Our optical microscope and tracking algorithm has a position and orientation precision of ±13nm and ±0.004 rad and an accuracy of ±32nm and ±0.006 rad respectively. It shows the robustness of our tracking algorithm which finds the center of body (CoB) of the asymmetric boomerangs given by the cross point of the two boomerang arms [Figure 5.1.1(c)]. The CoB is used as a convenient tracking point (TP). We identify the orientation $\theta$ of the boomerang in each video frame as the angle bisector of the two arms. The position of the center of hydrodynamics (CoH) is shown in the schematic Figure 5.1.1(c). $\vec{r} = \vec{r}_1 + \vec{r}_2$ is the vector from the CoH to the TP. Methods for identification of the CoH are discussed later. The angle between the vector $\vec{r}$ and the symmetry axis $X_1$ is denoted as $\varphi$. Similar to chapter 2 and chapter 3 the frames collected from 200 videos were merged into single trajectory by shifting and rotating the coordinates of the first frame in the second video and matching it with the last frame of first video [65].

5.2 Lab Frame Measurements

5.2.1 Short Time and Long Time Diffusion Coefficients

In chapter 3 we showed that unlike ellipsoids which have two planes of symmetry in two dimensions, the MSDs of symmetric boomerang with one plane of symmetry grow
Figure 5.2.1 (a) MSDs of the CoB in the lab frame vs. $t$. Red dash line: the best linear fit for $t < 10$ s; dark brown line: theoretical fit using Eq. (5.4). (b) MSDs for the CoB in the lab frame with $\theta_0 = 0$. Red lines: theoretical curves with Eq. (5.3).
linearly with time only at short and long time [64]. In the intermediate crossover regime the MSDs are nonlinear. Similar to the symmetric boomerangs, for the asymmetric boomerangs with no symmetry planes in two dimensions, the motion is isotropic that is the MSDs along the lab frame axes \( x_1 \) and \( x_2 \) are identical. The MSDs are linear with time at short and long time with an intermediate crossover region [Figure 5.2.1(a)]. The short time diffusion coefficient \( \bar{D}^{ST} = 0.0375 \, \mu m^2/s \) is obtained by best linear fitting with data up to \( t = 10 \, s \). Linear fitting of the MSD at long time yields the long time diffusion coefficient \( \bar{D}^{LT} = 0.0225 \, \mu m^2/s \). The intermediate time shows a sub-diffusive regime.

Due to particle asymmetry it is expected that the diffusion of asymmetric boomerangs should be anisotropic owing to their direction dependent hydrodynamic resistance as seen in the case of ellipsoids [6] and also in symmetric boomerangs [64] in chapter 3. This behavior can be observed for asymmetric boomerangs if the average is done for trajectories with fixed initial orientations. Therefore as seen in Figure 5.2.1(b) when the initial orientations are fixed at \( \theta_0=0 \) the measured MSDs are anisotropic at short time and the particles diffuses faster along lab frame axes \( x_1 \) than along \( x_2 \) at short times. However at long time the diffusion coefficients become same as the directional memory is lost. It is to be noted that similar to symmetric boomerangs as seen in Chapter 3, the MSD along \( x_1 \) has a higher value than that along \( x_2 \) at long time.

### 5.2.2 Non-Zero Mean Displacements

For symmetric boomerangs with one plane of symmetry in two dimensions, the motion is biased towards the CoH. Consequently the mean displacement is non-zero for
Figure 5.2.2 (a) Mean Displacement of the CoB along $x_1$ and $x_2$ direction in the lab frame for fixed initial orientation with $\theta_0 = 0$. Red lines: theory curves with Eq. (5.2).
fixed initial orientation. This phenomenon is more generic and can be observed for any particle when the TP is not coincident with the CoH. Hence for asymmetric boomerangs where the CoH lies outside the body, the MDs are non-zero for a fixed initial orientation when CoB is used as the TP. As seen in Figure 5.2.2 when the initial angle fixed at $\theta_0=0$ the MD is non-zero along both the $x_1$ and $x_2$ axis at short time. The MDs saturates out at long time as the average position of the TP reaches the CoH. For random initial orientations of the particle motion is isotropic and hence the MDs in different directions average out and go to zero.

### 5.2.3 Langevin Theory and Comparison with Experiments

In a similar approach to that of Chapter 3, assuming that the asymmetric boomerangs in two dimensions possess a CoH, we can write the position of the TP [Figure 5.1.1(c)] as a vector sum of the position of CoH and the vector $\mathbf{r}$ from CoH to the TP

$$
\mathbf{x}(t) = \mathbf{x}^{CoH}(t) - r\cos[\theta(t) + \phi]\hat{x}_1 - r\sin[\theta(t) + \phi]\hat{x}_2
$$

(5.1)

where $\mathbf{r}$ is the vector from the CoH to the TP, $\theta(t)$ is the angle bisector of the boomerang arms and the angle between the angle bisector line and $\mathbf{r}$ is given by $\phi$ which is a constant. At the CoH the translational-rotational motion is decoupled hence similar to an ellipsoid [6] the diffusion of CoH is characterized by two translation diffusion coefficients $D_{22}^{CoH}$, $D_{11}^{CoH}$ and a single rotational diffusion coefficient $D_\theta$ in two dimensions. Similar to Chapter 3 by superposing the ellipsoidal motion of CoH and that
of the vector \( r \) the MDs and MSDs of the TP for fixed initial angle \( \theta_0 \) can be derived as [see Appendix]:

\[
\langle \Delta x_i(t) \rangle_{\theta_0} = r a_i \tau_1(t) 
\]

\[
\langle [\Delta x_i(t)]^2 \rangle_{\theta_0} = 2D^{CoH} t + \cos(2(\theta_0 + \phi)) r^2/2 + \Delta D/4D_\theta b_i \tau_4(t) + 2r^2a_i^2 \tau_1(t)
\]  

(5.2) (5.3)

where \( \tau_n = 1 - \exp(-nD\theta t) \), \( a_1 = \cos(\theta + \phi) \), \( a_2 = \sin(\theta + \phi) \), \( b_1 = -1 \), \( b_2 = 1 \),

\[
\overline{D}^{CoH} = (D_{11}^{CoH} + D_{22}^{CoH})/2, \ \Delta D = D_{22}^{CoH} - D_{11}^{CoH} .
\]

For \( \theta_0 = 0 \) the body frame coincides with the lab frame axes and from Eq. (5.2) we get the MDs along the lab frame axes as \( \langle \Delta x_1(t) \rangle_{\theta_0} = r \cos \phi \tau_1(t) = r \tau_1(t) \) and \( \langle \Delta x_2(t) \rangle_{\theta_0} = r \sin \phi \tau_1(t) = r \tau_1(t) \) hence the MDs along \( x_1 \) and \( x_2 \) are biased in the direction of \(-r_1\) and \(-r_2\) respectively and saturates out at long time as seen in Figure 5.2.2. Consequently on an average the CoB moves towards the CoH. The experimental results are in good agreement with the analytical results as seen Figure 5.2.1 and Figure 5.2.2. However the angle averaged MDs goes to zero as the MDs in different directions average out.

Averaging Eq. (5.3) over different initial angle \( \theta_0 \) we obtain the angle averaged MSD in the lab which is the same as that of the symmetric boomerangs and expressed as:

\[
\langle [\Delta x_{1,2}(t)]^2 \rangle = 2\overline{D}^{CoH} t + r^2 \tau_1(t)
\]

(5.4)

From Eq. (5.4) the short-time diffusion coefficient obtained as \( \overline{D}^{ST} = \overline{D}^{CoH} + r^2D_\theta/2 \), that depends on the position of the TP. In the long time the diffusion is independent of the TP and same as that of the CoH \( \overline{D}^{LT} = \overline{D}^{CoH} \).
This suggests that the crossover behavior from short time faster to log time slower diffusion observed for both the symmetric and asymmetric boomerangs is universal and should be observed for any particle as long as the tracking point is not coincident with the CoH. The characteristic crossover time is given by the rotational diffusion coefficient, \( \tau_\theta = 1/(2D_\theta) \) which is independent of the frame of reference in two dimensions.

To estimate the proper value of the diffusion coefficient in the lab frame knowledge of the position of the CoH is essential. As seen in Chapter 3 for the symmetric boomerang the CoH is located at a distance \( r = D_{2\theta}/D_\theta \) on the symmetric axis from the tracking point which is taken to be CoB [64]. \( D_{2\theta} \) is the coupled diffusion coefficient that can be measured in the body frame. Since for the asymmetric boomerang there is no plane of symmetry in two dimensions [Figure 5.1.1(c)] the translational motion along both the body frame axes gets coupled with rotation. Hence the CoH is displaced from the \( X_1 \) axis by \( r_2 \) along the \( X_2 \) direction. The distance of the CoH from the origin of the body frame in the \( X_1 \) direction is given by \( r_1 \). Therefore the distance of the CoH from the tracking point can be obtained from the simple geometry as

\[
    r = \sqrt{r_1^2 + r_2^2} \quad (5.5)
\]

and the angle \( \phi \) made by the vector \( r \) with the \( X_1 \) axis is given by

\[
    \phi = \tan^{-1} \frac{r_2}{r_1} \quad (5.6)
\]

5.3 Measurement of the Diffusion Matrix in the Body Frame

To measure the body frame diffusion coefficients the displacements in the lab frame were transformed into the body frame through a rotational transformation
Figure 5.3.1 (a) MSDs vs. $t$ along the $X_1$ and $X_2$ axes in the body frame. (b) Translation-rotation correlations vs. $t$ along $X_1$ and $X_2$ axes. (c) Correlations between translations along $X_1$ and $X_2$ directions. (d) MSD of $\theta$ vs. $t$. The red lines are the best linear fittings with small time data.
where \( i, j = 1 \) or 2, and \( R_{ij}(\theta_n) \) is the transformation matrix and we use \( \theta_n = \frac{\theta(t_n) + \theta(t_{n+1})}{2} \) which corresponds to a continuous body frame [64] as discussed in chapter 3. The displacements in each time step are accumulated as \( X_i(t_n) = \sum_{k=0}^{n} \Delta X_i(t_k) \) to obtain the body frame trajectory.

The translational and rotational diffusion coefficients in the body frame are calculated by linear fitting of the translational and rotational means square displacements. Similar to Chapter 3 the MSDs can be analytically derived as [see Appendix]

\[
\left\langle \Delta X_i^2(t) \right\rangle = 2D_{11}t = 2\left(D_{11}^{\text{CoH}} + r_2^2D_{\theta} \right)t \tag{5.8}
\]

\[
\left\langle \Delta X_2^2(t) \right\rangle = 2D_{22}t = 2\left(D_{22}^{\text{CoH}} + r_1^2D_{\theta} \right)t \tag{5.9}
\]

\[
\left\langle \Delta \theta^2(t) \right\rangle = 2D_{\theta}t \tag{5.10}
\]

The measured MSDs in the \( X_1 \) and \( X_2 \) directions are linear with time and the diffusion coefficients calculated from the slopes are \( D_{11} = 0.025 \) \( \mu \text{m}^2/\text{s} \) and \( D_{22} = 0.05 \) \( \mu \text{m}^2/\text{s} \) [Figure 5.3.1(a)]. The angular MSD is also linear with time with rotational diffusion coefficient \( D_{\theta} = 0.033 \) \( \text{rad}^2/\text{s} \) [Figure 5.3.1(d)].

The off diagonal elements of the diffusion matrix correspond to the coupling of translational displacements along \( X_1 \) and \( X_2 \) with each other and with the rotational displacements. The coupling correlations can be derived as [see Appendix]
The correlations functions calculated in the body frame for translational and rotational displacements are linear with coupled diffusion coefficients $D_{12} = 0.0075 \text{ \mu m}^2/\text{s}$, $D_{20} = -0.0305 \text{ \mu m}\cdot\text{rad}/\text{s}$, $D_{10} = -0.0095 \text{ \mu m}\cdot\text{rad}/\text{s}$ respectively [Figure 5.3.1(b-c)]. From Eq. 5.11-5.13 we can write $D_{12} = D_{10}D_{2\theta}/D_{\theta}$. Therefore in 2D, out of nine only five elements of the diffusion matrix are independent for the asymmetric boomerangs.

### 5.4 Locating the Center of Hydrodynamics

Previous theories predict the location of CoH for symmetric boomerang to be somewhere on the symmetry axis [24]. Therefore the CoH was located by calculating the diffusion coefficients for TPs along the symmetry axis [64] for symmetric boomerangs in chapter 3. Unlike symmetric boomerangs, to locate the CoH for asymmetric boomerang the TP is shifted in the two dimensional plane of $X_1$-$X_2$ and the diffusion coefficients are measured. Figure 5.4.1 shows the measured diffusion coefficients in the $X_1$-$X_2$ plane with the origin at CoB projected along one axis. The variation of $D_{11}$ and $D_{10}$ along $X_2$ axis can be derived from Eq. (5.8) and Eq. (5.12) as $D_{11} = D_{11}^{CoH} + r_2^2D_{\theta}$ and $D_{1\theta} = r_2D_{\theta}$ respectively. For a given position on the $X_2$ axis $D_{11}$ and $D_{10}$ are constants along $X_1$ [Figure 5.4.1(a-b)]. Similarly we obtain from Eq. (5.9) and Eq. (5.13) the variation of $D_{22}$ and $D_{2\theta}$ along $X_1$ axis, given as $D_{22} = D_{22}^{CoH} + r_1^2D_{\theta}$ and $D_{2\theta} = r_1D_{\theta}$ [Figure 5.4.1(d-e)].
Figure 5.4.1  (a-c) Measured $D_{11}$ (a), $D_{10}$ (b) and $D_{12}$ (c) as a function of the tracking point position in the $X_2$ direction for fixed values of $X_1$ coordinate. Positions of the $X_1$ coordinate are shown in the inset. Red lines in (a) and (b) are fits with Eq. (5.8) and Eq. (5.12). (d-f) Measured $D_{22}$ (d), $D_{20}$ (e) and $D_{12}$ (f) as a function of tracking point position in the $X_1$ direction for fixed values of $X_2$ coordinate. Values of the $X_2$ coordinate are shown in the inset. Red lines in (d) and (e) are fits with Eq. (5.9) and Eq. (5.13). Red lines in (c) and (f) derived from Eq. (5.11).
$D_{12}$ as a function of position is obtained from Eq. (5.11) as $D_{12} = r_1r_2D_\theta$. Keeping position on $X_1$ axis fixed the variation of $D_{12}$ along $X_2$ is shown in Figure 5.4.1(c) and the variation along $X_1$ with $X_2$ fixed is shown in Figure 5.4.1(f). Figure 5.4.1 shows that the theoretical results (red lines) are in good agreements with experiments.

At the CoH the translational diffusion coefficients are minimum and the coupled diffusion is zero. $D_{11}$ is minimum and $D_{1\theta}$ goes to zero at a distance $d_{2}^{CoH} = 0.29\mu m$ from the origin along $X_2$. Also $d_{2}^{CoH}$ is given by $d_{2}^{CoH} = D_{1\theta}/D_\theta$. $D_{12}$ also goes to zero at the same point along $X_2$ [Figure 5.4.1]. It is to be noted that that at the same point $D_{22}$ is not at its minimum and $D_{2\theta}$ is non-zero. $D_{22}$ is minimum and $D_{2\theta}$ goes to zero at a distance $d_{1}^{CoH} = 0.86\mu m$ from the origin along $X_1$. $D_{12}$ also goes to zero at the same point along $X_1$ [Figure 5.4.1]. On the other hand, $d_{1}^{CoH}$ can be derived from the relation $d_{1}^{CoH} = D_{2\theta}/D_\theta$. Therefore the CoH for the asymmetric boomerang is located at $(d_{1}^{CoH}, d_{2}^{CoH})$ from the origin on the $X_1$-$X_2$ of plane with CoB as the origin. In our measurements the origin was fixed at CoB. Using Eq. (5.5) and Eq. (5.6) we can get the distance of the CoH from the tracking point as $r = \sqrt{D_{2\theta}^2 + D_{1\theta}^2}/D_\theta = 0.9\mu m$ and $\varphi = \tan^{-1} D_{2\theta}/D_{1\theta} = 17.85^\circ$.

5.5 Summary

In conclusion, we have shown that for asymmetric boomerangs CoH exist if the boomerang diffusion is restricted in a two dimensional plane. Since the CoH lies outside the body the diffusion is faster at short time and crosses over to a slower diffusion regime
at long time. The short time diffusion coefficients in the lab frame are dependent on the TP similar to the symmetric boomerangs. We further show that for fixed initial orientation the motion is biased towards the CoH and the mean displacements (MD) are non-zero along both the lab frame axes. In the body frame the translational displacements along both the axes are coupled with rotation. Moreover as there is no symmetry plane in two dimensions, the translational displacements along the two body frame axes are correlated and asymmetric boomerangs in two dimensions has translational-translational coupling diffusion coefficient along with the translational, rotational and translational-rotational coupled diffusivities. Therefore for bodies with no symmetry in two dimensions a fourth diffusion coefficient corresponding to translational-translational coupling is required to characterize their motion. Since asymmetric boomerangs have no plane of symmetry in two dimensions, our findings can be extended to bodies of any arbitrary shape which does not have a screw like symmetry. For these kinds of complex shapes there is no preferential tracking point and the position of the CoH is hitherto unknown. By analyzing the diffusion coefficients for any tracking point fixed on the body and thereby recalculating the same for tracking points on a two dimensional plane the CoH can be located in two dimensions.
CHAPTER 6

SUMMARY AND CONCLUSIONS

The latest state-of-the-art micro-fabrication techniques allow us to fabricate colloidal particles of predefined shapes and sizes. Boomerang particles with different arm lengths and variable apex angles were fabricated using projection lithography system from UV curable polymeric photo resists [64]. Video microscopy technique and single particle tracking was used to study the diffusion of the boomerangs in two dimensions. We wrote our own tracking algorithm to locate the position and orientation of the particles with very high precision and accuracy. It is an extension of the algorithm for tracking spherical particles considering it as a point spread function. We have generalized it for the case of boomerangs and it can be further extended for tracking other irregular shapes.

Our experimental observations show that the diffusion of boomerang is drastically different from those highly symmetric particles like spheres and ellipsoids. This is a major contribution to the field as most naturally occurring rigid bodies are of irregular shape and there is no obvious tracking point as most often the center of mass (CoM) does not lie at the center of body. For symmetric bodies like spheres and ellipsoids the CoM is coincident with the CoH and hence tracking the CoM yields a linear MSD vs. time relationship. However this is not true in general and for boomerangs the mean-square displacements (MSD) are only linear at short and long times with a distinct cross-over
regime. The MSD exhibit a crossover from short time faster to long time slower diffusion with the short-time diffusion coefficients dependent on the points used for tracking [64]. We have also showed that the mean displacements are biased towards the center of hydrodynamic stress (CoH) due to the translation-rotation coupling. A model based on Langevin theory elucidates that these behaviors are ascribed to the superposition of two diffusive modes: the ellipsoidal motion of the CoH and the rotational motion of the tracking point with respect to the CoH. The CoH can be located by analyzing the diffusion coefficients of any tracking point located on the body of the particle. Our experimental results show that CoH always exists for both symmetric and asymmetric boomerangs in two dimensions.

The single particle tracking experiments on the boomerangs also allowed us to investigate the effect of translation-rotation coupling on the underlying statistical nature of their distribution function. We found that displacement probability distribution of Brownian boomerangs is non-Gaussian yet Fickian at short time and becomes Gaussian at very long time. However, the probability functions at both the long and short times collapse to a master curve. In the intermediate time regime the boomerang motion is sub-diffusive and the distribution functions are non-scalable. We showed that this behavior arises from the translation-rotation coupling owing to the non-coincidence of the tracking point with the CoH.

Since boomerangs represents a class of rigid bodies of more generals shape, therefore our findings are generic and true for any non-skewed particles in two dimensions. Recent years have seen an upsurge in the synthesis and manufacturing of
colloids with extraordinary control on shape, size, interactions and functionalities. Therefore our effort in this direction is a significant step forward towards understanding the diffusion of irregularly shaped colloids. Our results not only have important implications for studying the diffusion and transport of anisotropic particles but also raise fundamental questions about their underlying distribution function. Since previous theories have predicted skewed behaviors for boomerangs in three dimensions [27], it will be worthwhile to explore in our future experiments the cross over from non-skewed behaviors in two dimensions to skewed behaviors in three dimensions of the boomerangs. Moreover by engineering particle shapes, microswimmers may be tailored to perform circular, spinning-top or other types of motion [53-55]. Understanding the hydrodynamics of chiral particles may lead to new avenues towards separation of particle or molecular enantiomers [87].
APPENDIX

The theoretical calculations were done by Andrew Konya and Dr. Jonathan V. Selinger. These have been included here for better understanding of the thesis.

A1 Langevin Theory for the Boomerang with Equal Arms

As pointed out by Brenner and others [23-28, 64], the center of hydrodynamic stress (CoH) is located on particle’s symmetric lines. Assuming that the CoH for the boomerang is located at \( (x_1^{CoH}, x_2^{CoH}) \) on the bisector of the apex angle, then the position of a tracking point (TP) on the symmetry line is simply the sum of the CoH position vector and the vector \( r = -r \cos \theta \hat{k}_1 - r \sin \theta \hat{k}_2 \) from the CoH to the TP:

\[
\begin{bmatrix}
  x_1(t) \\
  x_2(t)
\end{bmatrix} = \begin{bmatrix}
  x_1^{CoH}(t) \\
  x_2^{CoH}(t)
\end{bmatrix} - r \begin{bmatrix}
  \cos \theta(t) \\
  \sin \theta(t)
\end{bmatrix}
\] (A1)

where \( \theta(t) \) is the orientation of the particle. Therefore the motion of the TP can be described by:

\[
\begin{bmatrix}
  \dot{x}_1(t) \\
  \dot{x}_2(t)
\end{bmatrix} = \begin{bmatrix}
  \dot{x}_1^{CoH}(t) \\
  \dot{x}_2^{CoH}(t)
\end{bmatrix} + r \begin{bmatrix}
  \sin \theta(t) \\
  -\cos \theta(t)
\end{bmatrix} \dot{\theta}(t)
\] (A2)

Since the displacements of \( x^{CoH} \) and \( r \) are not correlated, i.e., \( \langle [\Delta x^{CoH}(t)] [\Delta r(t)] \rangle = 0 \), the mean displacements (MDs) and mean square displacements (MSDs) of the TP can be written as:
\[ \langle \Delta \xi_i(t) \rangle = \langle \Delta \xi_i^{\text{CoH}}(t) \rangle + \langle \Delta \eta_i(t) \rangle \]  \hspace{1cm} (A3) 

\[ \langle [\Delta \xi_i(t)]^2 \rangle = \langle [\Delta \xi_i^{\text{CoH}}(t)]^2 \rangle + \langle [\Delta \eta_i(t)]^2 \rangle \]  \hspace{1cm} (A4) 

A1.1 Lab Frame Results

According to the definition of the CoH, the diffusion tensor and the resistance tensor for the CoH are diagonalized. Therefore, under over-damped conditions, the inertial term in the Langevin equation can be neglected, and the Langevin Equations for the CoH under no external force in the body frame can be written in 2D as:

\[
\begin{pmatrix}
\zeta_{xx}^{\text{CoH}} & 0 & 0 \\
0 & \zeta_{yy}^{\text{CoH}} & 0 \\
0 & 0 & \zeta_{\theta\theta}^{\text{CoH}}
\end{pmatrix}
\begin{pmatrix}
\dot{X}_1^{\text{CoH}}(t) \\
\dot{X}_2^{\text{CoH}}(t) \\
\dot{\theta}(t)
\end{pmatrix} =
\begin{pmatrix}
\zeta_{xx}(t) \\
\zeta_{yy}(t) \\
\zeta_{\theta\theta}(t)
\end{pmatrix}
\]  \hspace{1cm} (A5)

where \( \zeta_{ij}^{\text{CoH}} \) is the hydrodynamic resistance tensor. The Gaussian random noise \( \xi_i(t) \) is related to the resistance tensor through the fluctuation-dissipation theorem:

\[ \langle \xi_i(t) \rangle = 0 \]
\[ \langle \xi_i(t) \xi_j(t') \rangle = 2k_BT \zeta_{ij}^{\text{CoH}} \delta(t-t') \]

Here \( i, j = 1, 2, \theta \). The diffusion tensor follows the generalized Einstein-Smoluchowski relationship: \( D_{ij}^{\text{CoH}} = k_BT \left( \zeta_{ij}^{\text{CoH}} \right)^{-1} \). Eq. (A5) can be rewritten as \( \dot{X}_i^{\text{CoH}} = \frac{1}{k_BT} D_{ij}^{\text{CoH}} \dot{\xi}_j(t) \)

For simplification, we scale the random noise as: \( \xi_j(t) = k_BT \sqrt{2/D_{ij}^{\text{CoH}}} \eta_j(t) \), where \( \eta_i(t) \) is a random variable with a normal Gaussian distribution, i.e. \( \langle \eta_i(t) \rangle = 0 ; \langle \eta_i(t) \eta_j(t') \rangle = \delta_{ij} \delta(t-t') \). The Langevin Equation can then be written separately for the translational and rotational components as:
The equations of motion in the lab frame are obtained through a rotation transformation of the body frame Eq. (A6):

\[
\begin{pmatrix}
\dot{X}_1^{\text{CoH}}(t) \\
\dot{X}_2^{\text{CoH}}(t)
\end{pmatrix} = \begin{pmatrix}
\sqrt{2D_{11}^{\text{CoH}}} & 0 \\
0 & \sqrt{2D_{22}^{\text{CoH}}}
\end{pmatrix} \eta(t)
\]

(A6)

\[
\dot{\theta}(t) = \sqrt{2D_{\theta}} \eta_{\theta}(t)
\]

(A7)

These Langevin equations (A6), (A7) and (A8) are the same as those for an ellipsoidal particle whose solutions have been given in Ref. [6]. It can be easily seen that the MDs of the CoH for fixed initial angle \( \theta_0 \) are zero:

\[
\langle [\Delta X_1^{\text{CoH}}(t)]_{\theta_0} \rangle = \langle [\Delta X_2^{\text{CoH}}(t)]_{\theta_0} \rangle = 0
\]

(A9)

Using the results in Ref. [6], the MSDs of the CoH with fixed initial orientation \( \theta_0 \) take the form:

\[
\langle [\Delta X_1^{\text{CoH}}(t)]^2 \rangle_{\theta_0} = \cos^2 \theta_0 \left( D_{11}^{\text{CoH}} + D_{22}^{\text{CoH}} \right) t - \frac{\Delta D^{\text{CoH}}}{4D_{\theta}} (1 - e^{-4D_{\theta} t})
\]

\[
+ \sin^2 \theta_0 \left( D_{11}^{\text{CoH}} + D_{22}^{\text{CoH}} \right) t + \frac{\Delta D}{4D_{\theta}} (1 - e^{-4D_{\theta} t})
\]

(A10)

\[
\langle [\Delta X_2^{\text{CoH}}(t)]^2 \rangle_{\theta_0} = \cos^2 \theta_0 \left( D_{11}^{\text{CoH}} + D_{22}^{\text{CoH}} \right) t + \frac{\Delta D^{\text{CoH}}}{4D_{\theta}} (1 - e^{-4D_{\theta} t})
\]

\[
+ \sin^2 \theta_0 \left( D_{11}^{\text{CoH}} + D_{22}^{\text{CoH}} \right) t - \frac{\Delta D}{4D_{\theta}} (1 - e^{-4D_{\theta} t})
\]

(A11)

where \( \Delta D = D_{22}^{\text{CoH}} - D_{11}^{\text{CoH}} \)
Displacement of vector $\mathbf{r}$

The displacements of $\mathbf{r}$ along the $x_1$ and $x_2$ directions can be expressed as:

$$\Delta r_1(t) = r \cos \theta - r \cos \left[ \theta_0 + \Delta \theta(t) \right]$$  \hspace{1cm} (A12)

$$\Delta r_2(t) = r \sin \theta - r \sin \left[ \theta_0 + \Delta \theta(t) \right]$$  \hspace{1cm} (A13)

Given that $\Delta \theta(t)$ has a Gaussian distribution with a zero mean, it can be shown that for integer $n$, $\langle \sin[n \Delta \theta(t)] \rangle = 0$, and $\langle \cos[n \Delta \theta(t)] \rangle = \exp(-n^2 D_\theta \tau)$. The MDs of the vector $\mathbf{r}$ then become:

$$\langle \Delta r_1(t) \rangle_{\theta_0} = r \cos \theta_0 \left( 1 - e^{-D_\theta \tau} \right)$$  \hspace{1cm} (A14)

$$\langle \Delta r_2(t) \rangle_{\theta_0} = r \sin \theta_0 \left( 1 - e^{-D_\theta \tau} \right)$$  \hspace{1cm} (A15)

The MSDs of $\mathbf{r}$ are derived as the following:

$$\langle [\Delta r_1(t)]^2 \rangle_{\theta_0} = r^2 \cos^2 \theta_0 - 2 r^2 \cos \theta_0 \langle \cos[\theta_0 + \Delta \theta(t)] \rangle + \frac{r^2}{2} \langle 1 + \cos 2[\theta_0 + \Delta \theta(t)] \rangle$$

Or

$$\langle [\Delta r_1(t)]^2 \rangle_{\theta_0} = \frac{1}{2} r^2 \cos^2 \theta_0 \left( 3 - 4 e^{-D_\theta \tau} + e^{-4 D_\theta \tau} \right) + \frac{1}{2} r^2 \sin^2 \theta_0 \left( 1 - e^{-4 D_\theta \tau} \right)$$  \hspace{1cm} (A16)

Similarly,

$$\langle [\Delta r_2(t)]^2 \rangle_{\theta_0} = \frac{1}{2} r^2 \sin^2 \theta_0 \left( 3 - 4 e^{-D_\theta \tau} + e^{-4 D_\theta \tau} \right) + \frac{1}{2} r^2 \cos^2 \theta_0 \left( 1 - e^{-4 D_\theta \tau} \right)$$  \hspace{1cm} (A17)

MD and MSD of the Tracking Point

Substituting Eq. (A9) and Eq. (A14)-(A15) into Eq. (A3) yields the MDs of the TP with fixed initial angle $\theta_0$:
\[ \langle \Delta x_1(t) \rangle_{\theta_0} = r \cos \theta_0 (1 - e^{-D_0 t}) \]  
(A18)

\[ \langle \Delta x_2(t) \rangle_{\theta_0} = r \sin \theta_0 (1 - e^{-D_0 t}) \]  
(A19)

Substituting Eq. (A10)-(A11) and Eq. (A16)-(A17) into Eq. (A4) yields the MSDs of the TP for fixed initial orientation \( \theta_0 \):

\[ \langle [\Delta x_1(t)]^2 \rangle_{\theta_0} = \cos^2 \theta_0 \left[ 2D_{\text{CoH}}^t t - \frac{AD}{4D_0} \left( 1 - e^{-4D_0 t} \right) + \frac{r^2}{2} \left( 3 - 4e^{-D_0 t} + e^{-4D_0 t} \right) \right] + \sin^2 \theta_0 \left[ 2D_{\text{CoH}}^t t + \frac{AD}{4D_0} \left( 1 - e^{-4D_0 t} \right) + \frac{r^2}{2} \left( 1 - e^{-4D_0 t} \right) \right] \]  
(A20)

\[ \langle [\Delta x_2(t)]^2 \rangle_{\theta_0} = \sin^2 \theta_0 \left[ 2D_{\text{CoH}}^t t - \frac{AD}{4D_0} \left( 1 - e^{-4D_0 t} \right) + \frac{r^2}{2} \left( 3 - 4e^{-D_0 t} + e^{-4D_0 t} \right) \right] + \cos^2 \theta_0 \left[ 2D_{\text{CoH}}^t t + \frac{AD}{4D_0} \left( 1 - e^{-4D_0 t} \right) + \frac{r^2}{2} \left( 1 - e^{-4D_0 t} \right) \right] \]  
(A21)

where \( D_{\text{CoH}}^t = (D_{12}^{\text{CoH}} + D_{22}^{\text{CoH}}) / 2 \).

Specifically, when the CoB is used as the TP with \( \theta_0 = 0 \), and \( r \) represents the distance of the CoH from the CoB, the MDs are simplified as:

\[ \langle \Delta x_1(t) \rangle_{\theta_0=0} = r \left( 1 - e^{-D_0 t} \right) \]  
(A22)

\[ \langle \Delta x_2(t) \rangle_{\theta_0=0} = 0 \]  
(A23)

And the MSDs are simplified as:

\[ \langle [\Delta x_1(t)]^2 \rangle_{\theta_0=0} = 2D_{\text{CoH}}^t t - \left( \frac{AD}{4D_0} + \frac{r^2}{2} \right) \left( 1 - e^{-4D_0 t} \right) + 2r^2 \left( 1 - e^{-4D_0 t} \right) \]  
(A24)

\[ \langle [\Delta x_2(t)]^2 \rangle_{\theta_0=0} = 2D_{\text{CoH}}^t t + \left( \frac{AD}{4D_0} + \frac{r^2}{2} \right) \left( 1 - e^{-4D_0 t} \right) \]  
(A25)
Averaging Eq. (A22)-(A23) and Eq. (A24)-(A25) over different initial orientation \( \theta_0 \) yields the angle averaged MDs and MSDs in the lab frame:

\[
\langle A\xi_1(t) \rangle = \langle A\xi_2(t) \rangle = 0
\]

\[
\langle [A\xi_1(t)]^2 \rangle = \langle [A\xi_2(t)]^2 \rangle = 2D_{\text{CoH}}t + r^2(1 - e^{-D_\eta t})
\]

(A26) (A27)

Eq. A27 indicates that the averaged diffusion coefficient of the CoB in the lab frame is

\[
\overline{D}^{ST} = \overline{D}^{\text{CoH}} + \frac{1}{2} r^2 D_\eta \quad \text{for short times and} \quad \overline{D}^{LT} = \overline{D}^{\text{CoH}} \quad \text{for long time.}
\]

A1.2 The Two Body Frames

Since the displacements obtained from the trajectories are in the lab frame, a rotation transformation needs to be performed to determine the elements of the diffusion tensor. We start with velocities in the body frame which are related to those in the lab frame through:

\[
\begin{align*}
\dot{X}_1(t) &= \cos \theta'(t) \dot{X}_1(t) + \sin \theta'(t) \dot{X}_2(t) \\
\dot{X}_2(t) &= -\sin \theta'(t) \dot{X}_1(t) + \cos \theta'(t) \dot{X}_2(t)
\end{align*}
\]

(A28)

where \( \theta'(t) \) is the angle used to transform the lab frame velocity (and displacements) into the body frame. To note, we use \( \theta'(t) \) to distinguish it from \( \theta(t) \). Using Eq. (A2) yields:

\[
\begin{align*}
\dot{X}_1(t) &= \dot{X}_1^{\text{CoH}}(t) + \sin [\theta(t) - \theta'(t)] r \alpha_\eta \dot{\eta}_\theta(t) = \dot{X}_1^{\text{CoH}}(t) + \dot{R}_1(t) \\
\dot{X}_2(t) &= \dot{X}_2^{\text{CoH}}(t) - \cos [\theta(t) - \theta'(t)] r \alpha_\eta \dot{\eta}_\theta(t) = \dot{X}_2^{\text{CoH}}(t) + \dot{R}_2(t)
\end{align*}
\]

(A29)

where \( \dot{R}_1(t) \) and \( \dot{R}_2(t) \) are the velocities of the vector \( r \) transformed into the body frame, and \( \dot{\theta}(t) = \sqrt{2D_\alpha \dot{\eta}_\theta(t)} = \alpha_\eta \dot{\eta}_\theta(t) \) from Eq. (A7). The MDs, MSDs and cross coupling of the TP in the body frame are simply:
In experiments, for the time interval between $t_n$ and $t_{n+1}$, one can choose either

$$\theta(t) = \frac{\theta(t_n) + \theta(t_{n+1})}{2},$$

which define a body frame noted here as the continuous body frame (CBF), or

$$\theta(t) = \theta(t_n),$$

which define another body frame noted here as the discrete body frame (DBF).

As shown in Ref. [6], these two body frames yield the same results for ellipsoidal particles. Since Eqs. (A6)-(A7) are the same to those for ellipsoids, we have

$$\langle \Delta X_i(t) \rangle = \langle \Delta X_i^{CoH}(t) \rangle + \langle \Delta R_i(t) \rangle$$

(A30)

$$\langle [\Delta X_i(t)]^T \rangle = \left\langle \left[ \Delta X_i^{CoH}(t) \right]^T \right\rangle + \left\langle [\Delta R_i(t)]^T \right\rangle$$

(A31)

$$\langle \Delta X_i(t) \Delta \theta(t) \rangle = \left\langle \Delta X_i^{CoH}(t) \Delta \theta(t) \right\rangle + \langle \Delta R_i(t) \Delta \theta(t) \rangle$$

(A32)

In the following we show theoretically that for boomerangs these two body frames yield different results due to different displacements of the vector $r$. This result implies that as long as the TP is not coincident with the CoH, these two body frames are different regardless of the particle shape.

**Motion of $r$ in the Body Frame**

From Eq. (A29), we rewrite the velocities of $r$ in the body frame as:
\[ \dot{R}_1(t) = \sin[\theta(t) - \theta'(t)] r \alpha_0 \eta_0(t) \]  
(A33)

\[ \dot{R}_2(t) = -\cos[\theta(t) - \theta'(t)] r \alpha_0 \eta_0(t) \]  
(A34)

For a time step between \( t_0 \) and \( t_0 + \tau \), the displacements of \( R_1 \) and \( R_2 \) are respectively

\[ \Delta R_1(\tau) = \int_{t_0}^{t_0 + \tau} dt' \sin[\theta(t') - \theta'(t')] r \alpha_0 \eta_0(t') , \quad \Delta R_2(\tau) = -\int_{t_0}^{t_0 + \tau} dt' \cos[\theta(t') - \theta'(t')] r \alpha_0 \eta_0(t'). \]

Due to the discretized nature of the experimental trajectories, \( \theta'(t') \) used in either the DBF or CBF is not the same as the instantaneous angle \( \theta(t') \). For small \( \tau \), \( \theta(t') - \theta'(t') \) is small, and the MDs can be expressed as:

\[ \langle \Delta R_1(\tau) \rangle = \left( \int_{t_0}^{t_0 + \tau} dt' [\theta(t') - \theta'(t')] r \alpha_0 \eta_0(t') \right) \]  
(A35)

\[ \langle \Delta R_2(\tau) \rangle = -\left( \int_{t_0}^{t_0 + \tau} dt' r \alpha_0 \eta_0(t') \right) = 0 \]  
(A36)

the MSDs of \( R_1 \) and \( R_2 \) can be expressed as:

\[ \langle [\Delta R_1(\tau)]^2 \rangle = r^2 \alpha_0^2 \left( \int_{t_0}^{t_0 + \tau} dt' [\theta(t') - \theta'(t')] \eta_0(t') \int_{t_0}^{t_0 + \tau} dt'' [\theta(t'') - \theta''(t'')] \eta_0(t'') \right) \]  
(A37)

\[ \langle [\Delta R_2(\tau)]^2 \rangle = \left( \int_{t_0}^{t_0 + \tau} dt' r \alpha_0 \eta_0(t') \int_{t_0}^{t_0 + \tau} dt'' r \alpha_0 \eta_0(t'') \right) \]  
(A38)

and the coupling with rotation for \( R_1 \) and \( R_2 \) can be expressed as:

\[ \langle \Delta R_1(\tau) \Delta \theta(\tau) \rangle = r^2 \alpha_0^2 \left( \int_{t_0}^{t_0 + \tau} dt' [\theta(t') - \theta'(t')] \eta_0(t') \int_{t_0}^{t_0 + \tau} dt'' \eta_0(t'') \right) \]  
(A39)

\[ \langle \Delta R_2(\tau) \Delta \theta(\tau) \rangle = \left( \int_{t_0}^{t_0 + \tau} dt' r \alpha_0 \eta_0(t') \int_{t_0}^{t_0 + \tau} dt'' r \alpha_0 \eta_0(t'') \right) \]  
(A40)
For a longer time \( t = n\tau \) with \( n \) being an integer, the displacements of \( r \) in the body frame are obtained by accumulating the displacements in individual time steps, i.e.

\[
\Delta R_{1,2}(t,t_0) = \sum_{i=0}^{n-1} \Delta R_{1,2}(\tau, t_0 + i\tau).
\]
The MDs, MSDs and the cross coupling displacements are then given by

\[
\langle \Delta R_{1,2}(t) \rangle = \left\langle \sum_{i=0}^{n-1} \Delta R_{1,2}(\tau, t_0 + i\tau) \right\rangle = n \langle \Delta R_{1,2}(\tau) \rangle \tag{A41}
\]

\[
\left\langle [\Delta R_{1,2}(t)]^2 \right\rangle = \left\langle \sum_{i=0}^{n-1} \Delta R_{1,2}(\tau, t_0 + i\tau) \right\rangle \left\langle \sum_{j=0}^{n-1} \Delta R_{1,2}(\tau, t_0 + j\tau) \right\rangle = \left\langle \sum_{i=0}^{n-1} \left[ \Delta R_{1,2}(\tau, t_0 + i\tau) \right]^2 \right\rangle + \left\langle \sum_{i\neq j} \Delta R_{1,2}(\tau, t_0 + i\tau) \Delta R_{1,2}(\tau, t_0 + j\tau) \right\rangle \tag{A42}
\]

\[
= n \left( \langle \Delta R_{1,2}(\tau) \rangle \right)^2 + (n^2 - n) \langle \Delta R_{1,2}(\tau) \rangle \langle \Delta R_{1,2}(\tau) \rangle
\]

\[
\langle \Delta R_{1,2}(t) \Delta \theta(t) \rangle = \left\langle \sum_{i=0}^{n-1} \Delta R_{1,2}(\tau, t_0 + i\tau) \right\rangle \left\langle \sum_{j=0}^{n-1} \Delta \theta(\tau, t_0 + j\tau) \right\rangle = n \langle \Delta R_{1,2}(\tau) \Delta \theta(\tau) \rangle \tag{A43}
\]

**Motion of \( r \) in the Continuous Body Frame (CBF)**

For the time interval between \( t_0 \) and \( t_0 + \tau \) in the CBF, \( \theta'(t') = \left[ \theta(t_0) + \theta(t_0 + \tau) \right] / 2 \).

Using the expressions \( \theta(t_0) = \theta(t') - \int_{t_0}^{t'} dt'' \dot{\theta}(t'') \) and \( \theta(t_0 + \tau) = \theta(t') + \int_{t'}^{t_0 + \tau} dt'' \dot{\theta}(t'') \), we have

\[
\theta'(t') = \theta(t') + \frac{\alpha_0}{2} \left[ \int_{t'}^{t_0 + \tau} dt'' \eta_o(t'') - \int_{t_0}^{t'} dt'' \eta_o(t'') \right] \tag{A44}
\]

Substituting Eq. (A44) into Eq. (A35), (A37) and Eq. (A39) lead to:
Based on Eq. (A38) and (A40), it can be shown that

\[ \langle [\Delta R_1(\tau)]^2 \rangle = 0 \] (A46)

\[ \langle [\Delta R_1(\tau)]^3 \rangle = 0 \] (A47)

\[ \langle [\Delta R_2(\tau)]^2 \rangle = 2r^2D_0\tau \] (A48)

\[ \langle [\Delta R_2(\tau)]^3 \rangle = 2rD_0\tau \] (A49)

Combining Eq. (A30), (A31), (A32), (A36), (A41), (A42), (A43), (A45), (A46), (A47), (A48) and (A49) leads to MDs, MSDS and cross coupling displacements of the TP in the CBF:

\[ \langle \Delta X_1(t) \rangle = 0 \] (A50)

\[ \langle \Delta X_2(t) \rangle = 0 \] (A51)

\[ \langle [X_1(t)]^2 \rangle = 2D_{11}^{\text{CoH}}t \] (A52)

\[ \langle [X_2(t)]^2 \rangle = 2(D_{22}^{\text{CoH}} + r^2D_0)t \] (A53)

\[ \langle X_1(t)\Delta \theta(t) \rangle = 0 \] (A54)

\[ \langle X_2(t)\Delta \theta(t) \rangle = 2rD_0t \] (A55)

**Motion of \( r \) in the Discrete Body Frame (DBF)**

In the DBF, \( \theta'(t') \) for the time interval between \( t_0 \) and \( t_0+\tau \) in Eq. (A33)-(A34) and Eq. (A36) can be expressed as:
\[ \theta'(t') = \theta(t_0) - \int_{t_0}^{t'} dt'' \dot{\theta}(t'') \quad (A56) \]

Substituting Eq. (A56) in Eq. (A35) gives:

\[
\langle \Delta R_1(t) \rangle = r \alpha_0 \int_{t_0}^{t_{0+\tau}} \int_{t_0}^{t_0+\tau} dt' \int_{t_0}^{t_0+\tau} dt'' \langle \eta_0(t') \eta_0(t'') \rangle
\]
\[
= 2rD_0 \int_{t_0}^{t_{0+\tau}} dt' \int_{t_0}^{t_0+\tau} dt'' \delta(t' - t'')
\]
\[
= rD_0 \tau
\quad (A57)
\]

Using Eq. (A56), Eq. (A37) can be evaluated as:

\[
\langle \Delta R_1^2(t) \rangle = r^2 \alpha_0 \int_{t_0}^{t_{0+\tau}} \int_{t_0}^{t_{0+\tau}} dt' \eta_0(t') \int_{t_0}^{t_{0+\tau}} dt'' \eta_0(t'') \int_{t_0}^{t_{0+\tau}} dt''' \eta_0(t''') \int_{t_0}^{t_{0+\tau}} dt'''' \dot{\theta}(t''''')
\]
\[
= 3r^2 D_0^2 \tau^2
\quad (A58)
\]

Using Eq. (A56), Eq. (A39) can be evaluated as:

\[
\langle \Delta R_1(t) \Delta \theta(t) \rangle = 0
\quad (A59)
\]

Based on Eq. (A38) and (A40) the MSD the cross coupling of \( R_2 \) in the DBF is the same as in the CBF:

\[
\langle [\Delta R_2(t)]^2 \rangle = 2r^2 D_0 \tau
\quad (A60)
\]
\[
\langle \Delta R_2(t) \Delta \theta(t) \rangle = 2rD_0 \tau
\quad (A61)
\]

Combining Eq. (A30), (A31), (A32), (A36), (A41), (A42), (A43), (A45), (A46), (A47), (A48) and (A49) leads to MDs, MSDS and cross coupling displacements of the TP in the DBF:
\[ \langle \Delta X_1(t) \rangle = rD_{\phi}t \quad (A62) \]

\[ \langle \Delta X_2(t) \rangle = 0 \quad (A63) \]

\[ \langle [X_1(t)]^2 \rangle = 2D_{11}^{\text{eff}}t + r^2 D_{\phi}^2 t^2 \quad (A64) \]

\[ \langle [X_2(t)]^2 \rangle = 2\left(D_{22}^{\text{eff}} + r^2 D_0\right)t \quad (A65) \]

\[ \langle X_1(t)\Delta \theta(t) \rangle = 0 \quad (A66) \]

\[ \langle X_2(t)\Delta \theta(t) \rangle = 2rD_{\phi}t \quad (A67) \]

A2  **Langevin Theory for the Boomerang with Asymmetric Arms.**

The MDs and MSDs for the asymmetric boomerang can be obtained exactly similar to that obtained for symmetric boomerang by replacing \( \theta \) with \((\theta + \phi)\).

**MD and MSD of the Tracking Point in the Lab Frame**

Since \( \phi \) is a constant from Eq. (A8) and (A9) the MDs are given by

\[ \langle \Delta x_1(t) \rangle_{\theta_0} = r \cos(\theta_0 + \phi)\left(1 - e^{-D_{\phi}t}\right) \quad (A68) \]

\[ \langle \Delta x_2(t) \rangle_{\theta_0} = r \sin(\theta_0 + \phi)\left(1 - e^{-D_{\phi}t}\right) \quad (A69) \]

From Eq. (A20) and (A21) the MSDs are derived as
\[ \langle [Ax_i(t)]^2 \rangle_{\theta_0} = \cos^2(\theta_0 + \phi) \left( 2D_{\text{CoH}} t - \frac{AD}{4D_0} \left( 1 - e^{-4D_0 \phi} \right) + \frac{r^2}{2} \left( 3 - 4e^{-D_0 \phi} + e^{-2D_0 \phi} \right) \right) + \sin^2(\theta_0 + \phi) \left( 2D_{\text{CoH}} t + \frac{AD}{4D_0} \left( 1 - e^{-4D_0 \phi} \right) + \frac{r^2}{2} \left( 1 - e^{-2D_0 \phi} \right) \right) \]  
(A70)

\[ \langle [Ax_2(t)]^2 \rangle_{\theta_0} = \sin^2(\theta_0 + \phi) \left( 2D_{\text{CoH}} t - \frac{AD}{4D_0} \left( 1 - e^{-4D_0 \phi} \right) + \frac{r^2}{2} \left( 3 - 4e^{-D_0 \phi} + e^{-2D_0 \phi} \right) \right) + \cos^2(\theta_0 + \phi) \left( 2D_{\text{CoH}} t + \frac{AD}{4D_0} \left( 1 - e^{-4D_0 \phi} \right) + \frac{r^2}{2} \left( 1 - e^{-2D_0 \phi} \right) \right) \]  
(A71)

Specifically, when the CoB as the TP with \( \theta_0 = 0 \), and \( r \) represents the distance of the CoH from the CoB, the MDs and MSDs are simplified as:

\[ \langle Ax_1(t) \rangle_{\theta_0} = r \cos \phi (1 - e^{-D_0 \phi}) = r_1 (1 - e^{-D_0 \phi}) \]  
(A72)

\[ \langle Ax_2(t) \rangle_{\theta_0} = r \sin \phi (1 - e^{-D_0 \phi}) = r_2 (1 - e^{-D_0 \phi}) \]  
(A73)

\[ \langle [Ax_1(t)]^2 \rangle_{\theta_0=0} = 2D_{\text{CoH}} t \cos (2 \phi) \left( \frac{AD}{4D_0} + \frac{r^2}{2} \right) (1 - e^{-4D_0 \phi}) + 2r^2 \cos^2 \phi (1 - e^{-D_0 \phi}) \]  
(A74)

\[ \langle [Ax_2(t)]^2 \rangle_{\theta_0=0} = 2D_{\text{CoH}} t \sin (2 \phi) \left( \frac{AD}{4D_0} + \frac{r^2}{2} \right) (1 - e^{-4D_0 \phi}) + 2r^2 \sin^2 \phi (1 - e^{-D_0 \phi}) \]  
(A75)

The angle averaged MDs and MSDs in the lab is obtained by averaging over different initial orientation \( \theta_0 \) and yields

\[ \langle Ax_1(t) \rangle = \langle Ax_2(t) \rangle = 0 \]  
(A76)

\[ \langle [Ax_1(t)]^2 \rangle = \langle [Ax_2(t)]^2 \rangle = 2D_{\text{CoH}} t + r^2 (1 - e^{-D_0 \phi}) \]  
(A77)
MDs, MSDs and Cross-Coupling in the Body Frame.

From Eq. (A33) and (A34) the motion of $\mathbf{r}$ in the body frame for asymmetric boomerangs is given by

$$
\dot{\mathbf{R}}_1(t) = \sin[\theta(t) - \theta'(t) + \varphi] r \alpha_\theta \eta_\theta(t)
$$

(A78)

$$
\dot{\mathbf{R}}_2(t) = -\cos[\theta(t) - \theta'(t) + \varphi] r \alpha_\theta \eta_\theta(t)
$$

(A79)

For continuous body frame (CBF) we have $\theta(t) = \theta'(t)$ and hence $\theta(t) - \theta'(t) = 0$, hence

$$
\dot{\mathbf{R}}_1(t) = \sin \varphi r \alpha_\theta \eta_\theta(t)
$$

(A80)

$$
\dot{\mathbf{R}}_2(t) = -\cos \varphi r \alpha_\theta \eta_\theta(t)
$$

(A81)

Therefore the MDs can be expressed as

$$
\langle [\Delta \mathbf{R}_1(\tau)]^2 \rangle = \sin \varphi \int_0^{\tau} dt' r \alpha_\theta \eta_\theta(t') = 0
$$

(A82)

$$
\langle [\Delta \mathbf{R}_2(\tau)]^2 \rangle = -\cos \varphi \int_0^{\tau} dt' r \alpha_\theta \eta_\theta(t') = 0
$$

(A83)

the MSDs of $R_1$ and $R_2$ can be expressed as:

$$
\langle [\Delta R_1(\tau)]^2 \rangle = \int_0^{\tau} dt' \int_0^{\tau} dt'' r \sin \varphi \alpha_\theta \eta_\theta(t') \alpha_\theta \eta_\theta(t'')
$$

(A84)

$$
= 2r^2 \sin^2 \varphi D_\theta \tau = 2r^2 \sin^2 \varphi D_\theta \tau
$$

$$
\langle [\Delta R_2(\tau)]^2 \rangle = \int_0^{\tau} dt' \int_0^{\tau} dt'' r \cos \varphi \alpha_\theta \eta_\theta(t') \alpha_\theta \eta_\theta(t'')
$$

(A85)

$$
= 2r^2 \cos^2 \varphi D_\theta \tau = 2r^2 \cos^2 \varphi D_\theta \tau
$$

and the coupling for $R_1$ and $R_2$ and with rotation can be expressed as:
\[
\langle \Delta R_1(\tau) \Delta \theta(\tau) \rangle = \left\langle \int_{t_0}^{t_0 + \tau} dt' r \sin \varphi \alpha_\theta \eta_\theta(t') \int_{t_0}^{t_0 + \tau} dt'' \alpha_\theta \eta_\theta(t'') \right\rangle 
\]
\[
= 2r \sin \varphi D_\theta \tau = 2r_1 D_\theta \tau 
\]  
(A86)

\[
\langle \Delta R_2(\tau) \Delta \theta(\tau) \rangle = -\left\langle \int_{t_0}^{t_0 + \tau} dt' r \cos \varphi \alpha_\theta \eta_\theta(t') \int_{t_0}^{t_0 + \tau} dt'' \alpha_\theta \eta_\theta(t'') \right\rangle 
\]
\[
= -2r \cos \varphi D_\theta \tau = -2r_1 D_\theta \tau 
\]  
(A87)

\[
\langle \Delta R_1(\tau) \Delta R_2(\tau) \rangle = -\left\langle \int_{t_0}^{t_0 + \tau} dt' r \sin \varphi \alpha_\theta \eta_\theta(t') \int_{t_0}^{t_0 + \tau} dt'' r \cos \varphi \alpha_\theta \eta_\theta(t'') \right\rangle 
\]
\[
= -2r^2 \sin \varphi \cos \varphi D_\theta \tau = -2r_1 r_2 D_\theta \tau 
\]  
(A88)

For a longer time with \( t = n\tau \) from Eq. (A84), (A85), (A86), (A87) and (A88) we have

\[
\langle\left|\Delta R_1(\tau)\right|^2\rangle = 2r_1^2 D_\theta \tau 
\]  
(A89)

\[
\langle\left|\Delta R_2(\tau)\right|^2\rangle = 2r_2^2 D_\theta \tau 
\]  
(A90)

\[
\langle \Delta R_1(\tau) \Delta \theta(\tau) \rangle = 2r_1 D_\theta \tau 
\]  
(A91)

\[
\langle \Delta R_2(\tau) \Delta \theta(\tau) \rangle = -2r_2 D_\theta \tau 
\]  
(A92)

\[
\langle \Delta R_1(\tau) \Delta R_2(\tau) \rangle = -2r_1 r_2 D_\theta \tau 
\]  
(A93)

Therefore similar to symmetric boomerang, combining the motion of CoH and \( r \) we get the MDs, MSDs and the cross correlations in the body frame as
\[ \langle \Delta X_1(t) \rangle = 0 \]  
\[ \langle \Delta X_2(t) \rangle = 0 \]  
\[ \langle [X_1(t)]^2 \rangle = 2\left(D_{22}^{\text{CoH}} + r_1^2 D_0 \right) t \]  
\[ \langle [X_2(t)]^2 \rangle = 2\left(D_{22}^{\text{CoH}} + r_2^2 D_0 \right) t \]  
\[ \langle X_1(t) \Delta \theta(t) \rangle = 2r_1 D_0 t \]  
\[ \langle X_2(t) \Delta \theta(t) \rangle = -2r_2 D_0 t \]  
\[ \langle X_1(t) X_2(t) \rangle = -2r_1 r_2 D_0 t \]
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