Brownian motion of a particle with arbitrary shape

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Abstract

Brownian motion of a particle with an arbitrary shape is investigated theoretically. Analytical expressions for the time-dependent cross-correlations of the Brownian translational and rotational displacements are derived from the Smoluchowski equation. The role of the particle mobility center is determined and discussed.

I. INTRODUCTION

Brownian motion of particles with arbitrary shapes has been recently investigated in many different contexts, including proteins, DNA, nanofibers, actins or other biological nano and micro objects [1–7]. There is a rapidly growing number of experimental and numerical studies, which give rise to interesting fundamental questions, challenging for theoreticians.

For nanoparticles, the characteristic time $\tau_R$ of the rotational Brownian diffusion is typically much smaller than the time resolution $t$ in the experiments, $t \gg \tau_R$. Therefore, they can be treated as point-like spherical particles, and described by the standard Brownian theory [8].

However, for Brownian microparticles, $\tau_R$ is of the order of seconds, and therefore non-negligible in comparison to the typical time scales of the measured Brownian motion, $t \lesssim \tau_R$. For example, in Ref. [7], the Brownian motion of a non-symmetric microparticle was investigated experimentally and numerically at the time scales comparable with the characteristic time $\tau_R$ of the rotational Brownian diffusion, and in this case the standard approach [8] is not sufficient. Therefore, the idea was to measure and model numerically the time-dependent cross-correlations of the Brownian translational and orientational displacements of microparticles with different shapes. These results were next also used to determine the mobility and friction matrices.

The goal of our work is to derive theoretically the explicit analytical expressions for cross-correlations of the Brownian translational and orientational displacements at all the time scales, and for arbitrarily shaped particles.

Parts of such a theoretical analysis have been already done. The motivation came from Ref. [4], focused on the problem of determining whether measurements of the self-diffusion coefficient and intrinsic viscosity of fibrinogen can be used to determine the protein configuration. Evaluation of both these quantities for particles with arbitrary shapes hinges on solving fundamental problems: what is the Brownian contribution to the intrinsic viscosity, and is the self-diffusion coefficient sensitive to the choice of a point on particle for which the mean square displacement is determined.

The expressions for the intrinsic viscosity of a Brownian non-symmetric particle were theoretically derived in Refs. [9, 10]. The relation between the Brownian mean square displacements of different points of a particle was determined in Ref. [11].

In this work, we consider a single Brownian particle of an arbitrary shape, in general non-isotropic and non-axisymmetric. Starting from the Smoluchowski equation [12–14], we develop a new formalism, which allows to determine the particle rotational and translational motion in a much simpler way as e. g. in Ref. [15], which is based on the Euler angles and Wigner functions.

Moreover, the essential result of this work is that using our new formalism, we derive simple explicit analytical expressions for the cross-correlations of the Brownian translational and rotational displacements. No such formulas have been known yet - instead, numerical Brownian simulations have been extensively used, as e. g. in Ref. [7].

II. SYSTEM AND ITS THEORETICAL DESCRIPTION

We consider an isolated Brownian particle of arbitrary shape immersed in an unbounded fluid of viscosity $\eta$ and temperature $T$. Its state will be described by $X = (R, \hat{\Omega})$, where $R$ is the position of the chosen particle point and $\hat{\Omega}$ describes the...
particle orientation, in particular in terms of the Euler angles which specify the orientation of the particle body-fixed axes with respect to the space-fixed axes. Probability distribution of finding the particle at time $t$ in state $X$ will be denoted by $P(X, t)$. It is normalized as

$$ \int dX \ P(X, t) = 1, \quad (1) $$

with

$$ dX = d\mathbf{R} \ d\mathbf{\Omega}, \quad (2) $$

and the element $d\mathbf{\Omega}$ defined in terms of the Euler angles in the same way as in Ref. [16] on page 161.

The evolution of the probability distribution $P(X, t)$ is governed by the Smoluchowski equation

$$ \frac{\partial}{\partial t} P(X, t) = \mathcal{L}(X) P(X, t) \quad (3) $$

with the Smoluchowski operator, which in the absence of external ambient flows, it results in the form

$$ \mathcal{L}(X) = \nabla_X \cdot \mathbf{D}(\hat{\Omega}) \cdot \nabla_X. \quad (4) $$

In the above equation,

$$ \nabla_X = \left( \frac{\partial}{\partial \mathbf{R}}, \frac{\partial}{\partial \alpha} \right), \quad (5) $$

with

$$ \frac{\partial}{\partial \mathbf{R}} = \left( \frac{\partial}{\partial R_1}, \frac{\partial}{\partial R_2}, \frac{\partial}{\partial R_3} \right), \quad (6) $$

$$ \frac{\partial}{\partial \alpha} = \left( \frac{\partial}{\partial \alpha_1}, \frac{\partial}{\partial \alpha_2}, \frac{\partial}{\partial \alpha_3} \right), \quad (7) $$

where $\alpha_k$ is the angle of rotation around the axis $k$.

Here and in the following, we denote the Cartesian indexes corresponding to $x, y, z$ by $k = 1, 2, 3$. According to the fluctuation-dissipation theorem [8], the $6 \times 6$ diffusion matrix $\mathbf{D}$ is proportional to the $6 \times 6$ mobility matrix $\mathbf{\mu}$,

$$ \mathbf{D}(\hat{\Omega}) = k_B T \ \mathbf{\mu}(\hat{\Omega}), \quad (8) $$

The mobility matrix $\mathbf{\mu}$ consists of four Cartesian $3 \times 3$ sub-matrices,

$$ \mathbf{\mu} = \begin{pmatrix} \mu_{tt} & \mu_{tr} \\ \mu_{rt} & \mu_{rr} \end{pmatrix}, \quad (10) $$

with the indices $t, r$ denoting the translational and rotational components, respectively. The $6 \times 6$ mobility matrix $\mathbf{\mu}$ is symmetric [18], therefore $\mu_{ij}^{rr} = \mu_{ij}^{rr}, \mu_{ij}^{rt} = \mu_{ij}^{rt}$. Therefore, the $3 \times 3$ matrices $\mu_{tt}$ and $\mu_{rr}$ are symmetric, but $\mu_{tr}$ in general is not symmetric. Analogical notation is adopted and the symmetry properties are held for the corresponding $3 \times 3$ sub-diffusion matrices, defined with the use of Eq. (5).

In general, the mobility matrix $\mathbf{\mu}$ depends on the choice of a reference center which is observed. The hydrodynamic mobility center is such a point for which the rotational-translational mobility matrix $\mathbf{\mu}^{rt}$ is symmetric. The position of this point is explicitly specified e.g. in Refs. [17] and [18].

Transformation relations between the mobility $\mathbf{\mu}_1$ for the reference center $\mathbf{r}_1$ and the mobility $\mathbf{\mu}_2$ for the reference center $\mathbf{r}_2$, called translational theorems for mobility matrices, are the following,

$$ \mathbf{\mu}_2^{rt} = \mathbf{\mu}_1^{rt} = \mathbf{\mu}^{rt}, \quad (11) $$

$$ \mathbf{\mu}_2^{tt} = \mathbf{\mu}_1^{tt} + \mathbf{\mu}^{rr} \times (\mathbf{r}_2 - \mathbf{r}_1), \quad (12) $$

$$ \mathbf{\mu}_2^{rr} = \mathbf{\mu}_1^{rr} - (\mathbf{r}_2 - \mathbf{r}_1) \times \mathbf{\mu}^{rr} \times (\mathbf{r}_2 - \mathbf{r}_1) \times (\mathbf{r}_2 - \mathbf{r}_1), \quad (13) $$

with the notation that for a second rank tensor $\mathbf{A}$ and a vector $\mathbf{V}$, one has

$$ [\mathbf{A} \times \mathbf{V}]_{ij} \equiv A_{ik} \epsilon_{ijk} V_i, \quad [\mathbf{V} \times \mathbf{A}]_{ij} \equiv \epsilon_{ijk} A_{kj}. \quad (14) $$

Here and later on, we use the Einstein’s summation convention, unless it is explicitly written that the repeating indices are fixed.

In particular, the translational theorems listed above can be applied to obtain the mobility matrices for an arbitrary reference center, if $\mathbf{\mu}_e$ for the hydrodynamic mobility center is known. The advantage of using this special center is not only the simplicity of the corresponding expressions. In Ref. [11] it has been shown that the hydrodynamic mobility center is especially meaningful for the translational diffusion process. In this work, we will show that such a reference center is also essential for the analysis of the cross-correlations of the Brownian translational or rotational displacements.

Taking into account the structure of the mobility and diffusion matrices, we split the Smoluchowski operator, defined in Eq. (8), into four parts,

$$ \mathcal{L} = \mathcal{L}^{tt} + \mathcal{L}^{tr} + \mathcal{L}^{rt} + \mathcal{L}^{rr}, \quad (15) $$
with

\[
\mathcal{L}^{tt} = \frac{\partial}{\partial R_k} D_{ij} \frac{\partial}{\partial R_j}, \quad (16)
\]

\[
\mathcal{L}^{rr} = \frac{\partial}{\partial \alpha_k} D_{ij}^{rr} \frac{\partial}{\partial \alpha_j}, \quad (17)
\]

\[
\mathcal{L}^{rt} = \frac{\partial}{\partial \alpha_k} D_{ij}^{rt} \frac{\partial}{\partial R_j}, \quad (18)
\]

\[
\mathcal{L}^{rr} = \frac{\partial}{\partial R_k} D_{ij}^{rr} \frac{\partial}{\partial \alpha_j}, \quad (19)
\]

In the above expressions for \( \mathcal{L}^{tt} \) and \( \mathcal{L}^{rr} \), the order of the diffusion coefficients and both derivatives can be interchanged. This property can be easily derived taking into account that \( D^{rt} \) does not depend on \( R \), and \( D^{rr} \) is symmetric. Below, we will show that for any second rank symmetric tensor \( S \),

\[
\frac{\partial}{\partial \alpha} \cdot S = 0. \quad (20)
\]

For the choice of the hydrodynamic mobility center, \( D^{rt} \) and \( D^{rr} \) are also symmetric and therefore in Eqs. (18)-(19) the order of all the operations is arbitrary.

We will now derive the relation (20). Let \( B \) be a tensor of rank \( n \). Suppose that \( B \) rotates with the particle, and the rotation matrix \( \mathcal{R} \) transforms an initial particle orientation \( \hat{\Omega}_0 \) to a final orientation \( \hat{\Omega} \). Then, the components \( B_{i_1i_2...i_n} \) of \( B \), with \( i_k = 1, 2, 3 \) for \( k = 1, ..., n \), change according to the formula,

\[
B_{i_1i_2...i_n}(\hat{\Omega}) = \mathcal{R}_{i_1j_1} \mathcal{R}_{i_2j_2}...B_{j_1j_2...j_n}(\hat{\Omega}_0), \quad (21)
\]

where \( \mathcal{R}_{ij} \) are the components of the rotation matrix \( \mathcal{R} \).

One can show \[7\] that

\[
\frac{\partial}{\partial \alpha_k} B_{i_1i_2...i_n} = \epsilon_{kj_1i_1} B_{j_1i_2...i_n} + \epsilon_{kj_2i_2} B_{i_1j_2...i_n} + ... \quad (22)
\]

It follows from the above that for a second rank symmetric tensor \( S \) the r.h.s. of Eq. (22) is equal to zero, what means that Eq. (20) is satisfied.

\section{III. BROWNIAN TRANSLATIONAL AND ROTATIONAL DISPLACEMENTS}

In this section, we will describe Brownian motion of a particle with an arbitrary shape. At time \( t=0 \) we choose an arbitrary particle point \( R(0) \) and orientation \( \hat{\Omega}(0) \), and we trace the positions \( R(t) \) and orientations \( \hat{\Omega}(t) \) at times \( t \).

We first analyze the time-dependent Brownian translational displacements,

\[
\Delta R = R(t) - R(0). \quad (23)
\]

We want to evaluate the dynamical cross-correlations,

\[
\langle \Delta R(t) \Delta R(0) \rangle = \int dX (R - R_0)(R - R_0)P(R, \hat{\Omega} \mid R_0, \hat{\Omega}_0; t). \quad (24)
\]

The average \( \langle ... \rangle_0 \) is taken with respect to the particle positions \( R \) and orientations \( \hat{\Omega} \) at time \( t \), with the conditional probability \( P(R, \hat{\Omega} \mid R_0, \hat{\Omega}_0; t) \), which takes into account that at \( t=0 \) the particle is located at \( R(0) = R_0 \), and oriented along \( \hat{\Omega}(0) = \hat{\Omega}_0 \). Actually, the average depends on \( R_0 \) and \( \hat{\Omega}_0 \) and formally, it should be explicitly denoted as \( \langle ... \rangle_{R_0,\hat{\Omega}_0} \), but we use a simpler notation \( \langle ... \rangle_0 \). The average is taken with respect to the conditional probability, which satisfies the Smoluchowski equation [4], i.e. it has the form

\[
P(R, \hat{\Omega} \mid R_0, \hat{\Omega}_0; t) = \exp(\mathcal{L}t)\delta(R - R_0)\delta(\hat{\Omega} - \hat{\Omega}_0). \quad (25)
\]

To determine change of the particle orientation \( \hat{\Omega} \), we follow Ref. [7] and at time \( t=0 \) we introduce three mutually perpendicular unit vectors \( u^{(p)}(0) = u_0^{(p)} \) which characterize the particle orientation, with \( p = 1, 2, 3 \), and we trace their evolution in time.

The orientation \( u^{(p)}(t), p = 1, 2, 3 \), at time \( t \) can be interpreted as the result of a rotation matrix \( \mathcal{R}(t) \), acting on the initial orientation \( u^{(p)}(0) \),

\[
u^{(p)}(t) = \mathcal{R}(t) \cdot u^{(p)}(0). \quad (26)
\]

With the use of the initial basis \( u^{(p)}(0) \), the components of the rotation matrix are expressed as \( \mathcal{R}_{pq} = u^{(p)}(0) \cdot u^{(q)}(t) \), with \( p, q = 1, 2, 3 \).

The matrix \( \mathcal{R} \) is orthogonal, i.e. \( \mathcal{R}^T = \mathcal{R}^{-1} \), where the superscript \( T \) stands for the transposition. We now decompose the rotation matrix into symmetric, \( \mathcal{R}^{(s)} \), and antisymmetric (skew-symmetric), \( \mathcal{R}^{(a)} \), parts, see Eqs. (A4)-(A5),

\[
\mathcal{R} = \mathcal{R}^{(s)} + \mathcal{R}^{(a)}. \quad (27)
\]

The antisymmetric part can be used to construct a vector, defined as

\[
\Delta u_k(t) = -\frac{1}{2} \epsilon_{kj} \mathcal{R}^{(a)}(t). \quad (28)
\]

This vector is parallel to the Euler rotation axis [19], with its length equal to the absolute value of the sinus of the rotation angle around this axis. From Eq. (28) it follows that

\[
\Delta u(t) = \frac{1}{2} \sum_{p=1}^3 u^{(p)}(0) \times u^{(p)}(t). \quad (29)
\]

Following Ref. [12], in this paper we use \( \Delta u(t) \) to describe the rotational Brownian motion. It is
good to keep in mind that the antisymmetric part \( R^{(a)} \) is not sufficient to describe all the properties of the rotation \( \Omega \).

The conditional probability of the occurrence of a given rotation has the form,

\[
P\left(\Omega \mid \Omega_0; t\right) = \int dR \ P\left(R, \hat{\Omega} \mid R_0, \hat{\Omega}_0; t\right). \quad (30)
\]

It satisfies the Smoluchowski equation with the initial condition \( P(\hat{\Omega}, t = 0) = \delta(\hat{\Omega} - \hat{\Omega}_0) \). Therefore,

\[
P\left(\hat{\Omega} \mid \hat{\Omega}_0; t\right) = \exp(\mathcal{L}_r^T t) \delta(\hat{\Omega} - \hat{\Omega}_0) \quad (31)
\]

The conditional probability \( P(\hat{\Omega} \mid \hat{\Omega}_0; t) \) depends only on the rotation matrix \( R \), which leads from \( \hat{\Omega}_0 \) to \( \hat{\Omega} \) (it does not depend on specific initial orientation \( \hat{\Omega}_0 \)). The Smoluchowski operator \( \mathcal{L}_r^T \) is self-adjoint \( [18] \), and the forward and backward Smoluchowski equations are the same. Therefore, the probability associated with \( R \) is equal to the probability associated with \( R^{-1} \). Saying it differently, this property follows from the detailed balance condition \( [9] \).

Taking this property into account, we conclude that the symmetric and antisymmetric parts of the rotation matrix are not correlated,

\[
\langle R^{(s)}(t) R^{(a)}(t) \rangle_0 = 0. \quad (32)
\]

To derive Eq. \( (32) \), we decompose \( R^{-1} = R^T \) into symmetric and antisymmetric parts,

\[
R^{-1} = R^{(s)} - R^{(a)},
\]

and use the relations

\[
\langle R^{(s)}(t) R^{(a)}(t) \rangle_0 = \langle (R^{-1})^{(s)}(t) (R^{-1})^{(a)}(t) \rangle_0 = -\langle R^{(s)}(t) R^{(a)}(t) \rangle_0 \quad (34)
\]

In Ref. \( [2] \), the Brownian motion was described based on measurements of the time-dependent 6 x 6 cross-correlation matrix,

\[
C(t) = \begin{bmatrix}
\langle \Delta R(t) \Delta R(t) \rangle_0 & \langle \Delta R(t) \Delta u(t) \rangle_0 \\
\langle \Delta u(t) \Delta R(t) \rangle_0 & \langle \Delta u(t) \Delta u(t) \rangle_0
\end{bmatrix}. \quad (35)
\]

The diffusion matrix \( D \) was determined as the time-derivative of the correlation matrix \( C(t) \) at time \( t = 0 \),

\[
\frac{1}{2} \left[ \frac{d}{dt} C(t) \right]_{t=0} = D, \quad (36)
\]

with the components, in analogy to Eq. \( (10) \), denoted as,

\[
D = \begin{bmatrix}
D^{tt} & D^{tr} \\
D^{rt} & D^{rr}
\end{bmatrix}. \quad (37)
\]

The relation Eq. \( (30) \) follows from the Smoluchowski equation \( [3] \).

In this work, we will describe Brownian motion of a particle with an arbitrary shape by deriving explicit analytical expressions for the cross-correlation matrix \( C(t) \) at all times \( t \). In general, \( C(t) \) depends on the choice of the reference center. The transformation relations for Eq. \( (35) \) to another reference center depend on both the antisymmetric and symmetric parts of the rotation matrix, \( R^{(a)} \) and \( R^{(s)} \), respectively. These relations will be discussed in Appendix \( [4] \).

IV. EVOLUTION DUE TO ROTATIONAL DIFFUSION

A. Tensors which rotate with the particle

While evaluating time-dependent cross-correlations, it is important to know how to determine changes due to the rotational diffusion. In this case, it is sufficient to average with respect to \( P(\hat{\Omega} \mid \hat{\Omega}_0; t) \), given by Eq. \( (31) \).

Therefore, we consider a tensor \( B \) which rotates with the particle and assume that \( \hat{\Omega}(t = 0) = \hat{\Omega}_0 \). For the conditional average of this tensor we find

\[
\langle B(t) \rangle_0 = \int d\hat{\Omega} \ B(\hat{\Omega}) \ P(\hat{\Omega} \mid \hat{\Omega}_0; t) = \int d\hat{\Omega} \ B(\hat{\Omega}) \ exp(\mathcal{L}_r^T t) \delta(\hat{\Omega} - \hat{\Omega}_0) = \exp(\mathcal{L}_r^T t) B(\hat{\Omega}) \bigg|_{\hat{\Omega} = \hat{\Omega}_0} \quad (38)
\]

The explicit form of the above average depends on the tensor rank. It can be relatively easily evaluated in the body-fixed frame in which the rotational diffusion tensor \( D^{rr} \) is diagonal,

\[
D_{ij}^{rr} = D_i \delta_{ij}, \quad \text{for given } i, j = 1, 2, 3. \quad (39)
\]

From now on, this frame will be used until the end of the paper.

The time-dependence of a tensor \( B \) follows from solving the eigenproblem for the Smoluchowski operator \( \mathcal{L}_r^T \), defined in Eq. \( (17) \). The eigenvalues depend on the rank of this tensor. For example, when the tensor rank is one (i.e. when \( B \) is a vector), we find three eigenvalues \(-f_i^{(1)}\) (as in Ref. \( [11] \)), with

\[
f_i^{(1)} = 3D_i - D_i, \quad i = 1, 2, 3, \quad (40)
\]

where

\[
D = \frac{1}{3} (D_1 + D_2 + D_3). \quad (41)
\]

Keep in mind that in this work, \( D_i \) and \( D \) always refer to the rotational-rotational diffusion (we skip the superscript \( ^{rr} \) for simplicity).
The corresponding eigenvectors are parallel to the principal axes of the operator $D^{rr}$. Denoting by $V_i(0)$ the components of this vector in the frame of reference in which $D^{rr}$ is diagonal at $t = 0$, and taking into account Eq. (48), we obtain,

$$
\langle V_i(t) \rangle_0 = \exp(-f_i^{(1)} t) V_i(0).
$$

For a second rank tensor $H(t)$, the problem was solved in Ref. [9], and the results are listed in Appendix A. The antisymmetric part of $H(t)$ may be associated with a vector, and therefore its evolution follows from Eq. (42), with the same eigenvalue $-f_i^{(1)}$, given by Eq. (40). The evolution of the traceless symmetric part of $H(t)$ is associated with five other eigenvalues, $-f_i^{(2)}$, $-f^{(+)}$ and $-f^{(-)}$, as the characteristic exponents in the time decay, where

$$
f_i^{(2)} = 3(D_i + D), \quad i = 1, 2, 3, \quad (43)
$$

$$
f^{(+)} = 6D + 2\Delta, \quad (44)
$$

$$
f^{(-)} = 6D - 2\Delta. \quad (45)
$$

with $D_i$ and $D$ defined in Eqs. (49) and (41) and

$$
\Delta = \sqrt{D_1^2 + D_2^2 + D_3^2 - D_1D_2 - D_1D_3 - D_2D_3}. \quad (46)
$$

The trace of $H(t)$ is a scalar and as such, it does not depend on time.

The expressions for the time-dependence of the average $\langle H(t) \rangle_0$, analogous to Eq. (42), are listed in Appendix A in Eqs. (A2)-(A3). The important outcome of our analysis is that these expressions contain different characteristic exponents, listed in Eqs. (40) and (43)-(45).

### B. Time scales of the rotational diffusion

From our analysis, outlined in the previous subsection, it follows that in general, there is no single characteristic time scale $\tau_R$ of the rotational self-diffusion. The exponents, listed in Eqs. (40) and (43)-(45), determine several characteristic time scales of the translational and rotational correlations,

$$
\tau^{(+)} = 1/f^{(+)}, \quad \tau^{(-)} = 1/f^{(-)},
$$

$$
\tau_i^{(1)} = 1/f_i^{(1)}, \quad \tau_i^{(2)} = 1/f_i^{(2)}, \quad (47)
$$

with $i = 1, 2, 3$. In general, these scales differ from each other, and a careful analysis of the time-dependence at long times is needed.

It is always true that $\tau_i^{(1)} \geq \tau_i^{(2)}$ and $\tau^{(-)} \geq \tau^{(+)}$, but $\tau_i^{(1)}$ can be smaller or larger than $\tau^{(-)}$, depending on the particle geometry.

### V. MEAN PARTICLE DISPLACEMENT

In general, due to the rotational diffusion, the mean particle displacement is not equal to zero i.e. if $R$ is the position of the chosen particle point $\langle \Delta R(t) \rangle_0 = \langle (R(t) - R(0))_0 \rangle_0 \neq 0$. To find this mean displacement let’s first consider special case when the point particle is the mobility center $R_C$.

Let’s calculate the time derivative of $\langle \Delta R_C(t) \rangle_0$. Taking into account the Smoluchowski equation [3] we have

$$
\frac{d}{dt} \langle \Delta R_C(t) \rangle_0 = \int dX \, (R_C - R_{C0}) \mathcal{L} P \left( R_C, \hat{\Omega} \bigg| R_{C0}, \hat{\Omega}_0; t \right). \quad (48)
$$

Now we will use the property, that for the mobility reference center, all the derivative can be shifted left. Then, integrations by parts give that the above derivative is equal to zero. Thus,

$$
\langle \Delta R_C(t) \rangle_0 = 0. \quad (49)
$$

Now consider the mean displacement for arbitrary chosen particle point $R$. The vector $R(t) - R_C(t)$ rotates with the particle. Thus from Eq. (42) we obtain

$$
\langle (R(t) - R_C(t))_{0,i} = (R(0) - R_C(0))_i \exp(-f_i^{(1)} t). \quad (50)
$$

and with (49) we get

$$
\langle \Delta R(t) \rangle_{0,i} = (R_C(0) - R(0))_i \left\{ 1 - \exp(-f_i^{(1)} t) \right\}. \quad (51)
$$

From Eq. (51) it follows that for long times, the mean position of an arbitrary point of the particle tends to the same limit: the initial position of the mobility center,

$$
\langle R(t) \rangle_0 \to R_C(0), \quad \text{for } t \to \infty. \quad (52)
$$

This result can be used to experimentally determine the particle mobility center, what is especially useful if the the location of $R_C(0)$ is not known in an analytical form.

In sections VI-VIII we will follow the motion of the mobility center, $R(t) \equiv R_C(t)$, chosen as the reference center in the mobility matrix, see Eqs. (11)-(13).

### VI. TRANSLATIONAL-TRANSLATIONAL CORRELATIONS

#### A. General expressions

Let us now consider correlations of a Brownian particle displacements, $\langle \Delta R_C(t) \Delta R_C(t) \rangle_0$. We remind that we stay in the reference frame in which $D^{rr}$ is diagonal and follow the motion of the mobility center $R_C$.
It is convenient to calculate first the time derivative of the expression \( (24) \):
\[
\frac{d}{dt} \langle \Delta R_C(t) \Delta R_C(t) \rangle_0 = \int dX \langle R_C - R_{C0} \rangle \langle R_C - R_{C0} \rangle \mathcal{L} P \left( \underbrace{R_C, \bar{\Omega}|R_{C0}, \bar{\Omega}_0}_{\text{c}} \right) \tag{53}
\]
Taking into account the explicit expressions \((16)-(19)\) for the Smoluchowski operator and interchanging the order of derivatives we obtain,
\[
\frac{d}{dt} \langle \Delta R_C(t) \Delta R_C(t) \rangle_0 = 2 \langle D^t(t) \rangle_0. \tag{54}
\]
We perform the above average using Eq. \((38)\). Since \(D^t\) is a symmetric tensor we get from Eq. \((A2)\) the following result for diagonal components,
\[
\frac{1}{2} \frac{d}{dt} \langle \Delta R_C(t) \Delta R_C(t) \rangle_{0,ii} = D^t + e^{-f(-)t} D^{tt}_t (-) + e^{-f(+)t} D^{tt}_t (+) \tag{55}
\]
where \(i = 1, 2, 3\) and
\[
D^t = \frac{1}{3} \Omega t. \tag{56}
\]
The meaning of the other symbols is explained in Appendix \(A\). After integration of Eq. \((55)\) with respect to \(t\) one obtains for \(i = 1, 2, 3\),
\[
\frac{1}{2} \langle \Delta R_C(t) \Delta R_C(t) \rangle_{0,ii} = D^t t + \frac{1-e^{-f(-)t}}{f(-)} D^{tt}_t (-) + \frac{1-e^{-f(+)t}}{f(+)} D^{tt}_t (+). \tag{57}
\]
The off-diagonal components \(i \neq j\) are given by
\[
\frac{1}{2} \frac{d}{dt} \langle \Delta R_C(t) \Delta R_C(t) \rangle_{0,ij} = e^{-f(+)t} D^{tt}_t. \tag{58}
\]
where \(k\) is the remaining third index, \(k \neq i,j\). After integration of Eq. \((58)\) with respect to \(t\) one obtains
\[
\frac{1}{2} \langle \Delta R_C(t) \Delta R_C(t) \rangle_{0,ij} = -\frac{1-e^{-f(-)t}}{f(-)} D^{tt}_t (-). \tag{59}
\]
In the limit of \(t \to 0\), the time derivative of the expressions \((57)-(59)\) approaches the corresponding elements of the diffusion matrix, in agreement with Eq. \((36)\).

From the relation \((57)\), taking into account that \(D^{tt}_t (+)\) and \(D^{tt}_t (-)\) are traceless, one derives the expression for the mean square displacement,
\[
\frac{1}{6} \langle \Delta R_C(t) \cdot \Delta R_C(t) \rangle = D^t t. \tag{60}
\]
In Eq. \((60)\), the subscript “0” associated with the averaging has been omitted, because the mean square displacement is a scalar, and therefore it does not depend on the orientation, and in particular, on the initial orientation \(\Omega_0\).

The mean square displacement of the mobility center, given in Eq. \((50)\), reproduces the result from Ref. \([11]\).

For long times, Eqs. \((57)\) and \((59)\) take the form,
\[
\frac{1}{2} \langle \Delta R_C(t) \Delta R_C(t) \rangle_{0,ii} = D^t t + \frac{1}{f(-)} D^{tt}_t (-) + \frac{1}{f(+)D^{tt}_t (+) + O(e^{-t/\tau(-)})}, \tag{61}
\]
\[
\frac{1}{2} \langle \Delta R_C(t) \Delta R_C(t) \rangle_{0,ij} = \frac{1}{f(k)} D^{tt}_{ij} + O(e^{-t/\tau(k)^{(2)}}). \tag{62}
\]
It is important to emphasize that there are constant non-vanishing terms in the above expressions.

### B. Special cases

For an axisymmetric particle, a frame is chosen where the rotational-rotational diffusion matrix is diagonal, with the coefficients
\[
D_1 = D_2 \neq D_3. \tag{63}
\]
The translational-translational diffusion matrix is also diagonal,
\[
D^{tt}_{ij} = D^t \delta_{ij}, \text{ for } i, j = 1, 2, 3, \tag{64}
\]
\[
D^t = D_2 \neq D_3. \tag{65}
\]
The diagonal correlations have the form,
\[
\frac{1}{2} \langle \Delta R_C(t) \Delta R_C(t) \rangle_{0,ii} = \frac{1}{f(-)} \frac{1-e^{-f(-)t}}{(D_1 t - D_3^t)}, \tag{66}
\]
for \(i=1,2,\) and
\[
\frac{1}{2} \langle \Delta R_C(t) \Delta R_C(t) \rangle_{0,33} = \frac{1}{9D_1} D^t \frac{1-e^{-f(-)t}}{18D_1} (D_1 t - D_3^t). \tag{67}
\]
The off-diagonal components vanish.

For a spherical particle, the rotational and translational diffusion tensors are isotropic,
\[
D_1 = D_2 = D_3 = D, \tag{68}
\]
\[
D^t = D_2^t = D_3^t = D^t, \tag{69}
\]
and
\[
\frac{1}{2} \langle \Delta R_C(t) \Delta R_C(t) \rangle_{0} = D^t I, \tag{70}
\]
where \(I\) is the identity tensor.
VII. ROTATIONAL-ROTATIONAL CORRELATIONS

A. General expressions

From Eq. (29) it follows that the rotational-rotational correlations read,

$$\langle \Delta u(t) \Delta u(t) \rangle_0 = \frac{1}{4} \sum_{p=1}^{3} \sum_{q=1}^{3} u_{ij}^{(p)} \times \left<u^{(p)}(t)u^{(q)}(t)\right>_0 \times u_{ij}^{(q)}. \quad (71)$$

The average $\langle \ldots \rangle_0$ in the above equation is evaluated based on the expressions provided in Appendix [A].

The off-diagonal elements vanish, and the diagonal elements, $i = 1, 2, 3$, are given by

$$\langle \Delta u(t) \Delta u(t) \rangle_{0,ii} = \frac{1}{6} - \frac{3(D - D_0) + D}{12\Delta} e^{-f^{(-)}t} - \frac{3(D - D_0) + D}{12\Delta} e^{-f^{(+)}t} - \frac{1}{4} e^{-f^{-2}t} + \frac{1}{4} e^{-f^{(1)}t}. \quad (72)$$

In the limit of $t \to 0$, the time derivative of the above expressions approaches the corresponding elements of the diffusion matrix, in agreement with Eq. (60).

For long times,

$$\lim_{t \to \infty} \langle \Delta u(t) \Delta u(t) \rangle_0 = \frac{1}{6} I. \quad (73)$$

This result can be also obtained as the average of Eq. (72) with the equilibrium distribution.

B. Special cases

For an axisymmetric particle, $D_1=D_2\neq D_3$, and

$$\langle \Delta u(t) \Delta u(t) \rangle_{0,11} = \langle \Delta u(t) \Delta u(t) \rangle_{0,22} = \frac{1}{6} - \frac{1}{6} e^{-D_1 t} - \frac{1}{6} e^{-D_2 t} + \frac{1}{4} e^{-(D_1 + D_2) t} + \frac{1}{4} e^{-(D_1 + D_3) t}, \quad (74)$$

$$\langle \Delta u(t) \Delta u(t) \rangle_{0,33} = \frac{1}{6} + \frac{1}{12} e^{-D_1 t} - \frac{1}{2} e^{-2D_1 t} + \frac{1}{4} e^{-2D_3 t}. \quad (75)$$

To describe the rotational self-diffusion of an axisymmetric particle, it is common [12] to trace the change of the particle orientation vector along the symmetry axis, in this paper denoted as $u^{(3)}(t)$. This vector rotates with the particle, and therefore its evolution follows from Eq. (22). Using this relation, we reproduce the standard formula [12],

$$\left\langle \left[ u^{(3)}(t) - u^{(3)}(0) \right]^2 \right\rangle = 2(1 - e^{-2D_1 t}). \quad (76)$$

For a spherical particle, $D_1=D_2=D_3=D$, and

$$\langle \Delta u(t) \Delta u(t) \rangle_0 = \left[ \frac{1}{6} - \frac{5}{12} e^{-6D_1 t} + \frac{1}{4} e^{-2D_1 t} \right] I. \quad (77)$$

VIII. ROTATIONAL-TRANSLATIONAL CORRELATIONS

A. General expressions

Using Eq. (29) we have,

$$\langle \Delta u(t) \Delta R(t) \rangle_0 = \sum_{p=1}^{3} u_{0}^{(p)} \times \left<u^{(p)}(t) \Delta R(t) \right>_0, \quad (78)$$

where, as before, $u_{0}^{(p)}$ with $p = 1, 2, 3$ are the unit vectors corresponding to the orientation $\Omega_0$, and we choose the body-fixed frame in which the rotational diffusion tensor $D^{rt}$ is diagonal.

As shown in Appendix [B],

$$\left<u^{(p)}(t) \Delta R(t) \right>_0 = -2 \int_0^t d\tau e^{-f^{(1)}(t-\tau)} \left\langle A^{(p)}(\tau) \right\rangle_0, \quad (79)$$

where the second rank tensor $A^{(p)}$ is given by

$$A^{(p)} = u^{(p)} \times D^{rt}. \quad (80)$$

We now decompose the tensor $A^{(p)}$ and determine $\langle A^{(p)}(t) \rangle_0$ for all its parts as described in Appendix [A]. The resulting expressions are plugged into Eq. (79), and the integration with respect to $\tau$ is performed.

We obtain the following diagonal Cartesian components of the rotational-translational correlations,

$$\langle \Delta u(t) \Delta R(t) \rangle_{0,ii} = \frac{D^{rt}_{ij} - D^{rt}_{ji}}{8} \left[ e^{-f^{(2)}(t)} - e^{-f^{(1)}(t)} \right]$$

$$D^{rt}_{kj} \left[ \frac{1}{2} t e^{-f^{(1)}(t)} \right], \quad (81)$$

where $i = 1, 2, 3$ and $j, k$ are the remaining second and third indices such that $j + k = 6 - i$.

The off-diagonal Cartesian components are,
\[ (\Delta u(t) \Delta R_C(t))_{0,ij} = -\frac{D^i_{ij}}{2} \left[ \frac{D_j - D_k + \Delta}{\Delta} \frac{e^{-f_k^{(-)}t} - e^{-f_j^{(-)}t}}{f^{(-)} - f_j^{(1)}} + \frac{D_k - D_j + \Delta}{\Delta} \frac{e^{-f_k^{(+)t} - e^{-f_j^{(+)t}}}}{f^{(+) - f_j^{(1)}}} \right], \]

where the remaining third index \( k = 6 - i - j \). The expression \( [82] \) is not symmetric in \( ij \), but its derivative at \( t = 0 \) is symmetric.

In the limit of \( t \to 0 \), the time derivative of the above expressions approaches the corresponding elements of the diffusion matrix, in agreement with Eq. \( [80] \). For long times,

\[ \lim_{t \to \infty} (\Delta u(t) \Delta R_C(t)) = 0. \tag{83} \]

**B. Special cases**

For an axisymmetric particle, \( D^{ir} \) is skew-symmetric [18]. Therefore, it vanishes if evaluated with respect to the mobility center. Taking this into account, we obtain from Eqs. \( [81]-[82] \) the simple result,

\[ (\Delta u(t) \Delta R_C(t))_0 = 0. \tag{84} \]

**IX. Conclusions**

In this work, we performed theoretical analysis of the Brownian motion of a particle with an arbitrary shape. We derived analytical expressions for the time-dependent cross-correlations of the displacements of the particle position and orientation. These results were written in the frame of reference in which the rotational-rotational diffusion tensor is diagonal at \( t = 0 \), and with the choice of the mobility center as the reference center. These results can be compared with experimental data, using the following procedure.

Based on measurements of the time-dependent orientation \( u^{(p)}(t) \), it is possible to determine the correlation tensor \( (\Delta u(t) \Delta u(t))_0 \) and find its principal axes. From our analysis it follows that they coincide with the principal axes of the rotational-rotational diffusion tensor. Therefore, to be compared with our theoretical expressions, the experimental data should be recalculated to this new frame of reference in which \( (\Delta u(t) \Delta u(t))_0 \) is diagonal.

The initial position of the mobility center \( R_C(0) \) can be determined experimentally by tracing in time the average position \( \langle R(t) \rangle_0 \) of any particle point, and using our finding that \( \langle R(t) \rangle_0 \to R_C(0) \) when \( t \to \infty \).

The transformation formulae for \( C(t) \) from the mobility center to another arbitrary point can be derived analytically, as described in Appendix C. However, the transformation formula for \( (\Delta R(t) \Delta R(t))_0 \) involves the symmetric part of the rotation matrix \( R^{(s)} \), which cannot be expressed in terms of \( C(t) \).

Our simple explicit analytical expressions for the correlations \( C(t) \), valid for the mobility reference center, can be compared with the experimental data, measured for an arbitrary reference center, using the following procedure. Once the principal axes of the rotational-rotational diffusion tensor are determined, and used as the new coordinate system, with the recalculated time-dependent orientation \( u^{(p)}(t) \), and the initial position of the mobility center \( R_C(0) \) is determined experimentally, this information can be used as follows. First, the difference between the initial position \( R(0) \) of an arbitrary reference center, traced in experiments, and \( R_C(0) \), can be expressed as a linear combination of the orientation vectors \( u^{(p)}(0) \),

\[ R(0) - R_C(0) = \sum_{p=1}^{3} a_p u^{(p)}(0), \tag{85} \]

and the coefficients \( a_p \) can be determined. Taking into account that \( R(t) - R_C(t) \) rotates with the particle, we can use the same coefficients \( a_p \) to evaluate \( R_C(t) \) as

\[ R_C(t) = R(t) - \sum_{p=1}^{3} a_p u^{(p)}(t), \tag{86} \]

Eq. \( [80] \) allows to express (the unknown) stochastic trajectory \( R_C(t) \) in terms of (the known) stochastic trajectory \( R(t) \) and orientation \( u^{(p)}(t) \). This allows to extract from the measured data the correlations of the Brownian displacements of the mobility center, in the frame in which the rotational-rotational diffusion matrix is diagonal, and compare with our theoretical expressions for the time-dependent cross-correlation matrix \( C(t) \) for the mobility center \( R_C(t) \).

In contrast to numerical simulations, the analytical expressions provided in this work allow to determine the cross-correlations exactly. The accuracy of theoretical expressions is especially important for times comparable to the characteristic time scales of the rotational diffusion, when the cross-correlations change significantly with time.
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Appendix A: Change of a second rank tensor due to the rotational diffusion

In Eqs. (42)-(49), we derived the time-dependence of a vector, which rotates with the particle. Now we will do the same for a second rank tensor.

Let \( \mathbf{H}(t) \) be any second rank tensor which rotates with the particle, with \( \mathbf{H} \equiv \mathbf{H}(0) \). From Eq. (68) it follows that time evolution of this tensor due to rotational diffusion only is given as

\[
\langle \mathbf{H}(t) \rangle_0 = \exp(\mathcal{L}^{rr} t) \mathbf{H},
\]

(A1)

The explicit expression for \( \mathbf{H}(t) \) follows from Eqs. (22) (see Ref. [3]). As in the whole paper, we adopt the frame of reference in which the rotational-rotational diffusion tensor is diagonal, as in Eq. (30). For the diagonal components we obtain,

\[
\langle \mathbf{H}(t) \rangle_{0,ii} = \frac{1}{3} \text{tr} \mathbf{H} + \exp(-f^+(t)) \mathbf{H}^{(+)}_{ii}
+ \exp(-f^-(t)) \mathbf{H}^{(-)}_{ii},
\]

(A2)

where the first term is a scalar, and as such, it does not change in time, and the characteristic exponents \( f^+(t) \) and \( f^-(t) \) are given in Eqs. (41)-(45).

For the off-diagonal components \( i \neq j \),

\[
\langle \mathbf{H}(t) \rangle_{0,ij} = \exp(-f_{ij}^{(1)} t) \mathbf{H}_{ij}^{(a)} + \exp(-f_{ij}^{(2)} t) \mathbf{H}_{ij}^{(s)}
\]

(A3)

where \( k \) is the remaining third index, \( k \neq i, j \), and the characteristic exponents \( f_{ij}^{(1)} \) and \( f_{ij}^{(2)} \) are given in Eqs. (10)-(13).

In Eq. (A3), we use the decomposition of a second rank tensor \( \mathbf{H} \) into symmetric and antisymmetric parts, defined as

\[
\begin{bmatrix}
\mathbf{H}^{(s)} \\
\mathbf{H}^{(a)}
\end{bmatrix}
_{ij} = \frac{1}{2} \left( \mathbf{H}_{ij} + \mathbf{H}_{ji} \right),
\]

(A4)

\[
\begin{bmatrix}
\mathbf{H}^{(s)} \\
\mathbf{H}^{(a)}
\end{bmatrix}
_{ij} = \frac{1}{2} \left( \mathbf{H}_{ij} - \mathbf{H}_{ji} \right).
\]

(A5)

In Eq. (A2), the symmetric diagonal part is further split into the isotropic part, \( \frac{1}{3} \text{tr} \mathbf{H} \delta_{ij} \), and the diagonal non-isotropic parts,

\[
\begin{bmatrix}
\mathbf{H}^{(\pm)} \\
\mathbf{H}^{(\mp)}
\end{bmatrix}
_{ii} = \frac{1}{2} \left( 3 \frac{D_i - D}{4} \Delta \right) \mathbf{H}_{ii} + \frac{1}{3} \text{tr} \mathbf{H}
\]

\[
\pm \frac{D_i - D}{4} \Delta \left( \mathbf{H}_{jj} - \mathbf{H}_{kk} \right).
\]

(A6)

Above, \( j \) and \( k \neq j \) are the remaining indices different than \( i \).

Appendix B: Rotational-translational correlations

Using Eq. (29), one can write

\[
\langle \mathbf{u}^{(p)}(t) \Delta \mathbf{R}_C(t) \rangle_0 = \int d\Omega u^{(p)}(\Omega) \int d\mathbf{R}_C (\mathbf{R}_C - \mathbf{R}_{C,0}) P(\mathbf{R}_C, \Omega | \mathbf{R}_{C,0}, \Omega_0; t).
\]

(B1)

\[
\int d\mathbf{R}_C (\mathbf{R}_C - \mathbf{R}_{C,0}) P(\mathbf{R}_C, \Omega | \mathbf{R}_{C,0}, \Omega_0; t)
= -2 \int_0^t d\tau \exp[\mathcal{L}^{rr}(t-\tau)] \frac{\partial}{\partial \Omega_0} \cdot \mathbf{D}^{rr} P(\Omega | \Omega_0; \tau).
\]

(B3)

We now insert the expression (B3) into Eq. (B1), take into account that the Smoluchowski operator is self-adjoint, and perform the integration by parts with respect to \( \alpha \). We benefit from choosing the frame of reference, in which \( \mathbf{D}^{rr} \) is diagonal, with

\[
\mathcal{L}^{rr} \mathbf{u}^{(p)} = -f_p^{(1)} \mathbf{u}^{(p)}.
\]
and we use the relations (14), (22) to write for a vector $\mathbf{V}$ and a matrix $\mathbf{A}$,
\begin{equation}
\frac{\partial \mathbf{V}_m}{\partial \alpha_k} A_{kn} = - (\mathbf{V} \times \mathbf{S})_{mn} .
\end{equation}
(B5)

Finally, using Eq. (35), we obtain Eq. (79).

**Appendix C: Shift of the reference center**

The correlations $\langle \Delta \mathbf{u}(t) \Delta \mathbf{u}(t) \rangle_0$ do not depend on the choice of the reference center. Indeed, they depend only on the rotational-rotational components of the diffusion tensor (or, equivalently, the mobility matrix). But these components do not depend on the choice of a reference center, as it follows from Eqs. (11)-(13).

In this appendix, we derive expressions which allow to transform the correlations of the rotational and translational Brownian displacements, $\langle \Delta \mathbf{u}(t) \Delta \mathbf{R}(t) \rangle_0$, from one reference center $\mathbf{R}_1$ to another, $\mathbf{R}_2$. We denote,
\begin{equation}
\mathbf{R}_2 = \mathbf{R}_1 + \mathbf{R}_{21}.
\end{equation}
(C1)

The difference $\mathbf{R}_{21}$ rotates with the particle, and therefore it can be expressed using the set of the orientation vectors $\mathbf{u}^{(p)}$, with $p = 1, 2, 3$,
\begin{equation}
\mathbf{R}_{21} = \sum_{p=1}^{3} a_p \mathbf{u}^{(p)}.
\end{equation}
(C2)

Therefore,
\begin{equation}
\Delta \mathbf{R}_2(t) = \Delta \mathbf{R}_1(t) + \sum_{p=1}^{3} a_p \left( \mathbf{u}^{(p)}(t) - \mathbf{u}^{(p)}(0) \right)
\end{equation}
(C3)

Since $\langle \Delta \mathbf{u}(t) \rangle_0 = 0$, the transformation of the rotational-translational correlations between the reference centers $\mathbf{R}_1$ and $\mathbf{R}_2$ has the form,
\begin{align}
\langle \Delta \mathbf{u}(t) \Delta \mathbf{R}_2(t) \rangle_0 &= \langle \Delta \mathbf{u}(t) \Delta \mathbf{R}_1(t) \rangle_0 + \\
&+ \sum_{p=1}^{3} a_p \left( \langle \Delta \mathbf{u}(t) \mathbf{u}^{(p)}(t) \rangle_0 \right)
\end{align}
(C4)

To determine the difference, we take into account that $\Delta \mathbf{u}(t)$ is proportional to $\mathbf{R}^{(a)}$, see Eq. (25), while according to Eq. (20), $\mathbf{u}^{(p)}(t)$ contains both $\mathbf{R}^{(a)}$ and $\mathbf{R}^{(s)}$,
\begin{equation}
\mathbf{u}^{(p)}(t) = \mathbf{R}^{(a)}(t) \cdot \mathbf{u}^{(p)}(0) + \mathbf{R}^{(s)}(t) \cdot \mathbf{u}^{(p)}(0).
\end{equation}
(C5)

However, as shown in Eq. (32), the symmetric and antisymmetric parts of the rotation matrix are not correlated. Therefore, owing to Eq. (25), the only contribution to $\mathbf{u}^{(p)}(t)$ in Eq. (C4) comes from
\begin{equation}
\mathbf{R}^{(a)}(t) \cdot \mathbf{u}^{(p)}(0) = \Delta \mathbf{u}(t) \times \mathbf{u}^{(p)}(0).
\end{equation}
(C6)

Therefore,
\begin{align}
\langle \Delta \mathbf{u}(t) \mathbf{u}^{(p)}(t) \rangle_0 &= \langle \Delta \mathbf{u}(t) \Delta \mathbf{u}(t) \rangle_0 \times \mathbf{u}^{(p)}(0),
\end{align}
(C7)

and we finally obtain the transformation relation,
\begin{align}
\langle \Delta \mathbf{u}(t) \Delta \mathbf{R}_2(t) \rangle_0 &= \langle \Delta \mathbf{u}(t) \Delta \mathbf{R}_1(t) \rangle_0 + \\
&+ \langle \Delta \mathbf{u}(t) \Delta \mathbf{u}(t) \rangle_0 \times \mathbf{R}_{21}(0).
\end{align}
(C8)

This relation can be used to transform the expressions (81)-(82), valid for the mobility center $\mathbf{R}_1 = \mathbf{C}$, to account for the rotational-translational correlations determined for an arbitrary center $\mathbf{R}_2$.

The analogical transformation relations for the translational-translational correlations $\langle \Delta \mathbf{R}(t) \Delta \mathbf{R}(t) \rangle_0$ contain also correlations involving $\mathbf{R}^{(s)}(t)$, and therefore they cannot be expressed only in terms of the correlations $\mathbf{C}(t)$, and as such, they are not practical if only $\mathbf{C}(t)$ is measured. However, these additional correlations, $\langle \Delta \mathbf{R}(t) \mathbf{u}^{(p)}(t) \rangle_0$ and $\langle \mathbf{u}^{(p)}(t) \mathbf{u}^{(q)}(t) \rangle_0$, can be also determined in experiments. In this case, the corresponding expressions would be useful and can be easily derived based on the framework constructed in this work.

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