Mean joint residence time of two Brownian particles in a sphere

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Abstract. We calculate the mean joint residence time of two Brownian particles in a sphere, for very general initial conditions. In particular, we focus on the dependence of this residence time as a function of the diffusion coefficients of the two particles. Our results can be useful for describing kinetics of bimolecular diffusion controlled reactions activated by catalytic sites.

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1. Introduction

Elementary reactive process between two molecules $A$ and $B$ usually begins when their relative positions satisfy certain relations. In the simplest case of two molecules with spherical symmetry, one may consider that the reactive process starts when the relative distance of their centres is equal to the range of their reactive potential. This is the case for instance in the celebrated model introduced by Smoluchowski [1] and improved by many authors [2]. In a more general model, for given values of the coordinates characterizing $A$, the reaction can only take place if the coordinates of $B$ are located inside a reactive region $\Gamma(A)$ which, obviously, can be fairly complicated.

The probability that $B$ has not reacted up to time $t$ is clearly connected to the residence time of $B$ inside $\Gamma(A)$ up to time $t$. This fact seems to have been first recognized by Wilemski and Fixman [3]. Indeed, in their seminal work, the inverse reaction rate constant for the $A + B \rightarrow B$ diffusion limited reactions is given by the mean residence time (RT) of the particle $B$ inside $\Gamma(A)$. We address the reader for more details to the works by Doi [4], Temkin and Yakobson [5], Zhou [6] and Rice [2]. The residence time inside a finite domain $S$ is defined as the total time $T(t)$ spent by the Brownian particle up to time $t$ within $S$: contrary to the first exit time of $S$, the RT accounts for an arbitrary number of exits from and enters into $S$. The properties of the RT for an individual Brownian particle have been extensively studied [7, 8, 9, 10, 11, 12, 13, 14].

The purpose of this paper is to develop the notion of residence time in the case of a reaction between two particles, activated by immobile catalytic sites. For such reactions, $A + B + C \rightarrow B + C$, where the specie $C$ stands for the catalytic sites, the calculation of the effective reaction rate in a Wilemski-Fixman kind approach actually involves several functionals of time which can be identified as RT of Brownian particles [15]. One of them is the mean time spent simultaneously by the two reactants $A$ and $B$ inside a reactive region centered on a catalytic site $C$, for which the RT is averaged over all initial positions of $A$ and $B$ inside the reactive region.

Recently [16], this kind of joint residence time properties has been studied for an arbitrary number $N$ of Brownian particles, but only in the two-dimensional situation and for very particular initial conditions. Here, we focus on the case of two particles ($N = 2$). First, it will be shown that the mean residence time can be calculated exactly for general initial conditions in the two dimensional case. Then, in order to obtain an explicit reaction rate for the reaction $A + B + C \rightarrow B + C$ in 3-d, we will also study the three dimensional situation when particles start inside the reactive region. We will show that the mean joint residence time of $A$ and $B$ on a site $C$ can be calculated explicitly in several situation of physical interest. It is remarkable, in particular, that this problem can be solved exactly in 3 dimensions for arbitrary initial positions of the reacting particles.
2. The model

We consider 2 independent Brownian particles diffusing in a $d$ dimensional space, with $d \geq 2$, and we assume that they can only react on an immobile catalytic site, which will be represented by the sphere $D(O, R)$ of center $O$ and of radius $R$. We note $r_j(t)$ the positions of these particles at time $t$ ($j = 1, 2$), $r_j(0)$ the initial positions, and $D_j$ the corresponding diffusion coefficients. We introduce $1_S$ the indicator function of the sphere $D(O, R)$, that is

$$1_S(r) = \begin{cases} 
1 & \text{if } r \in D(0, R) \\
0 & \text{otherwise}
\end{cases}$$

(1)

The joint occupation time of the sphere $D(O, R)$ is defined by

$$T(t) = \int_0^t dt' \left( \prod_{j=1}^2 1_S(r_j(t')) \right)$$

(2)

Thus, the mean joint occupation time at time $t$ is

$$\mu(t) = \langle T(t) \rangle = \int_0^t \left( \prod_{j=1}^2 \langle 1_S(r_j(t')) \rangle \right) dt'$$

(3)

that is

$$\mu(t) = \int_0^t 2 \prod_{j=1}^2 \left( \int dr_j 1_S(r_j) \frac{1}{(4\pi D_j t')^{d/2}} \exp \left( -\frac{||r_j - r_j(0)||^2}{4D_j t'} \right) \right) dt' $$

(4)

From now on, we will limit ourselves to the long time limiting value of $\mu(t)$, which will be simply denoted as $\mu$

$$\mu \equiv \lim_{t \to \infty} \mu(t) = \frac{1}{(16\pi^2 D_1 D_2)^{d/2}} \int_0^\infty dy y^{d-2} \prod_{j=1}^2 \left( \int dr_j 1_S(r_j) \exp \left( -y \frac{||r_j - r_j(0)||^2}{4D_j} \right) \right)$$

(5)

where we did the change of variables $y = 1/t'$ in the integral.

In the Wilemski-Fixman approach of the bimolecular reactions $A + B \rightarrow B$ [3, 4, 5], the quantity which is actually involved in the expression of the kinetic constant is the mean $RT \langle \mu \rangle$ of a fictive particle inside a reactive sphere of radius $r_A + r_B$, averaged over the initial position of the particle inside the region, diffusing with $D = D_A + D_B$. More precisely, the overall rate constant $k$ is given by the inverse addition law

$$\frac{1}{k} = \frac{1}{k_D} + \frac{1}{k_A}$$

(6)

where $k_D$ is the contribution due to diffusion of particles and $k_A$ is associated to the reactive process itself. It is shown that

$$k_D = \frac{V}{\langle \mu \rangle}$$

(7)

where $V$ is the reaction zone volume.
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Note that this Wilemski-Fixman approach actually appears as the leading order of a perturbative theory with respect to $k_A$ which, as an unperturbed motion, takes the propagation of independent particles\cite{17}. In the framework of this approximation, the mean residence time $\langle \mu \rangle$ is calculated by considering that the particles perform independent Brownian motions.

Our main purpose here is to compute the mean value $\langle \mu \rangle$ for the present catalytically activated reaction $A + B + C \rightarrow B + C$, which now involves two diffusing particles and a disjoint reactive region. Therefore, $\langle \mu \rangle$ will now be called the mean joint residence time inside a region. The sequel of the paper is structured as follows. In section 3 we present results concerning the case when all the particles are initially at the origin $O$. These expressions are valid for an arbitrary dimension of space $d$. Next, we study more general initial conditions in dimensions $d = 2$ and $d = 3$ which are the physically relevant dimensions of the problem. In section 4 we discuss the $d = 2$ situation in two special cases: firstly, when all the particles are at $t = 0$ on the boundary of the sphere $D(O, R)$. Secondly, when one of the two particles is initially at the origin while the other one can be everywhere. In section 5 we solve the $d = 3$ situation in full generality, that is for arbitrary initial conditions of the diffusing particles. Therefore, this result gives the mean joint residence time involved in the bimolecular reaction activated by catalytic sites, whereas the other initial conditions mentioned previously can be related to specific reactive processes.

3. d-dimensional case when the two particles are initially at the origin

Physically, this situation corresponds, for example, to a dissociation recombination catalytically induced reaction.

We start by integrating Eq. (5) over $y$, which leads, after rescaling of the spatial integration variables to

$$\mu = \frac{\sigma_d^2 R^2 \Gamma(d-1)}{\pi^d} I(D_1, D_2) \tag{8}$$

where

$$I(D_1, D_2) = \int_0^{1/\sqrt{4D_1}} dx \int_0^{1/\sqrt{4D_2}} dy \frac{x^{d-1} y^{d-1}}{(x^2 + y^2)^{d-1}} \tag{9}$$

and $\sigma_d$ is the area of the $d$-dimensional hypersphere of unit radius.

We now proceed to the calculation of $I(D_1, D_2)$. First, we write $I(D_1, D_2) = J(D_1, D_2) + J(D_2, D_1)$ with

$$J(D_1, D_2) = \int_D dx dy \frac{x^{d-1} y^{d-1}}{(x^2 + y^2)^{d-1}} \tag{10}$$

and $D$ is the domain $D = \{ x \in [0, \frac{1}{\sqrt{4D_1}}], y \in [0, \frac{1}{\sqrt{4D_2}}], y \leq \sqrt{\frac{D_1}{D_2}} x \}$.

Changing to the new variables $z = x$, $t = y/x$ in $J(D_1, D_2)$, we obtain

$$J(D_1, D_2) = \int_0^{1/\sqrt{4D_1}} dzz \int_0^{\sqrt{D_1/D_2}} dt \frac{t^{d-1}}{(1 + t^2)^{d-1}}$$
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\[ \frac{1}{8dD_1} \left( \frac{D_1}{D_2} \right)^{d/2} \binom{d}{2} \binom{d}{2} - \frac{D_1}{D_2} \]

(11)

\( \binom{1}{2} \) being the standard Gauss hypergeometric function.

Thus,

\[ \mu = \frac{\sigma^2 R^2 \Gamma(d-1)}{8d \pi^d} \left\{ \frac{1}{D_1} g \left( \frac{D_1}{D_2} \right) + \frac{1}{D_2} g \left( \frac{D_2}{D_1} \right) \right\} \]

(12)

where

\[ g(x) = x^{d/2} \binom{d/2}{d} - \frac{x}{d} \]

(13)

Using the expression \( \sigma_d = d \pi^{d/2} / \Gamma(1 + d/2) \) as well as the duplication formula

\[ \Gamma(d-1) = 2^{d-2} d \pi^{d/2} \]

(14)

we finally find

\[ \mu = \frac{R^2}{\sqrt{\pi}} \sigma^{d-1} \frac{\Gamma \left( \frac{d-1}{2} \right)}{\Gamma \left( \frac{d}{2} + 1 \right)} \left\{ \frac{1}{D_1} g \left( \frac{D_1}{D_2} \right) + \frac{1}{D_2} g \left( \frac{D_2}{D_1} \right) \right\} \]

(15)

Specializing to the dimensions \( d = 2 \) and \( d = 3 \), we get the following explicit expression of the mean residence time \( \mu \) as a function of \( R, D_1 \) and \( D_2 \):

- for \( d = 2 \) : \( g(x) = \ln(1 + x) \), thus

\[ \mu = \frac{R^2}{4} \left\{ \frac{1}{D_1} \ln \left( 1 + \frac{D_1}{D_2} \right) + \frac{1}{D_2} \ln \left( 1 + \frac{D_2}{D_1} \right) \right\} \]

(16)

This result has already been obtained in ref [16] by a slightly different approach.

- for \( d = 3 \) : \( g(x) = \frac{3}{2} \left[ \arctan(\sqrt{x}) - \frac{\sqrt{x}}{1 + x} \right] \), and

\[ \mu = \frac{R^2}{\pi} \left\{ \frac{1}{D_1} \arctan \left( \sqrt{\frac{D_1}{D_2}} \right) + \frac{1}{D_2} \arctan \left( \sqrt{\frac{D_2}{D_1}} \right) - \frac{1}{\sqrt{D_1 D_2}} \right\} \]

(17)

We now briefly comment on the expressions (16) and (17) in the special case when the particle 1 moves much faster than the particle 2, that is when \( D_1 \gg D_2 \).

In that case, the two dimensional expression Eq. (16) becomes

\[ \mu \sim \frac{R^2}{4D_1} \ln \left( \frac{D_1}{D_2} \right) \]

(18)

The form of this last result appears, from the physical point of view, to be very reasonable. As a first approximation, we can say that this joint occupation time is given by the joint occupation time before the first exit time of the slow particle out of the disc. This time is of order \( t_2 = \frac{R^2}{D_2} \). Meanwhile, the fast particle leaves the disc and comes back several times. The time spent at each return of the particle 1 inside the disc is of order \( t_1 = \frac{R^2}{D_1} \), and the order of magnitude of the number of returns at time \( t_2 \) of
the particle one inside the disc is given by \( \ln \left( \frac{t_2}{t_1} \right) \), in the limit of long \( t_2 \) times. As a consequence, we expect

\[
\mu \sim \frac{D_2}{D_1} t_1 \ln \left( \frac{t_2}{t_1} \right) \sim \frac{R^2}{D_1} \ln \left( \frac{D_1}{D_2} \right)
\]  

which reproduces the dependence of \( \mu \) as a function of the diffusion coefficients \( D_1 \) and \( D_2 \) given by Eq. 16.

Concerning the three dimensional expression Eq. (17), the limit \( D_1 \gg D_2 \) leads to

\[
\mu \sim \frac{D_2}{D_1} \frac{R^2}{2D_1}.
\]  

This is clearly the expected result: knowing that the three dimensional Brownian motion is transient and that the particle 2 leaves the sphere after a very long time, the mean joint residence time identifies itself to the residence time of the only particle 1, which is precisely given by \( \frac{R^2}{2D_1} \).

We now examine more general initial conditions, and we restrict ourselves to the physically important cases corresponding to the two-dimensional and three-dimensional situations.

4. Two-dimensional situation

Integrating first with respect to the angular variables in Eq. 14,

\[
\mu = \frac{1}{4D_1D_2} \int_0^\infty \frac{d}{d} \prod_{j=1}^2 \left( \int_0^R dr_j \frac{yRr_j}{2D_j} \exp \left( -\frac{1}{4D_j} y(r_j^2 + R^2) \right) \right)
\]

where \( I_0 \) stands for a modified Bessel function of zeroth order. We have not been able to compute explicitly this integral for arbitrary initial conditions, but only in special cases: the first one is the case when the two particles are initially on the boundary of the disc and the second one the case when one of the two particles is initially at the origin.

4.1. Case when the two particles are initially on the boundary of the disc

In that special case, the spatial integrations can be done explicitly.

\[
\int_0^R dr_j r_j I_0 \left( \frac{yRr_j}{2D_j} \right) \exp \left( -\frac{1}{4D_j} y(r_j^2 + R^2) \right)
= R^2 \exp \left( -\frac{yR^2}{4D_j} \right) \int_0^1 du_j u_j I_0 \left( \frac{yR^2 u_j}{2D_j} \right) \exp \left( -\frac{yR^2}{4D_j} \right)
= \frac{D_j}{y} \left( 1 - \exp \left( -\frac{R^2y}{2D_j} \right) I_0 \left( \frac{yR^2}{2D_j} \right) \right)
\]

where we have used the fact that

\[
\int_0^1 dx x e^{-ax^2} I_0(2ax) = \frac{1}{4a} \left( e^a - e^{-a} I_0(2a) \right)
\]  

\[(23)\]
Finally,

$$\mu = \frac{1}{4} \int_0^\infty \frac{dy}{y^2} \prod_{j=1}^2 \left( 1 - \exp \left( -\frac{R^2 y}{2D_j} \right) I_0 \left( \frac{yR^2}{2D_j} \right) \right)$$  \hspace{1cm} (24)

In the special case when the two particles have the same diffusion coefficient \(D_1 = D_2 = D\), this equation becomes

$$\mu = \frac{R^2}{8D} \int_0^\infty \frac{dt}{t^2} \left( 1 - e^{-t} I_0(t) \right)^2,$$  \hspace{1cm} (25)

where the last integral can be numerically evaluated as

$$\int_0^\infty \frac{dt}{t^2} \left( 1 - e^{-t} I_0(t) \right)^2 \approx 1.06 \hspace{1cm} (26)$$

4.2. Case when one of the two particles is initially at the origin

We consider now a more general situation corresponding to the case when one of the two particles is initially at the origin while the other one can be everywhere. This situation can be a simple model for a third order reaction between an immobile site \(C\) and particles 1 and 2, if \(C\) and particle 1 initially constitute a complex molecule which should be dissociated to react with a chemical species 2 (provided that the distances from 1 and 2 to \(C\) are less than \(R\)).

The residence time of 1 and 2 within the catalytic region is then

$$\mu = \frac{1}{4D_1D_2} \int_0^\infty dy \left( \int_0^R dr_1 r_1 \exp \left( -\frac{1}{4D_1} y r_1^2 \right) \right) \left( \int_0^R dr_2 r_2 I_0 \left( \frac{y r_2^2}{2D_2} \right) \exp \left( -\frac{1}{4D_2} y (r_2^2 + (r_2^{(0)})^2) \right) \right),$$  \hspace{1cm} (27)

We perform first the integral with respect to \(y\):

$$\int_0^\infty dy \exp \left[ -y \left( \frac{r_1^2}{4D_1} + \frac{r_2^2 + (r_2^{(0)})^2}{4D_2} \right) \right] I_0 \left( \frac{y r_2^2}{2D_2} \right) = \left[ \left( \frac{r_1^2}{4D_1} + \frac{r_2^2 + (r_2^{(0)})^2}{4D_2} \right)^2 - \frac{(r_2 r_2^{(0)})^2}{4D_2^2} \right]^{-1/2}$$  \hspace{1cm} (28)

Performing next the integration over \(r_2\) and lastly over \(r_1\), introducing the dimensionless variables \(x = \frac{r_2^{(0)}}{R}\) and \(w = \frac{D_2}{D_1}\), we find after straightforward but lengthy calculations that

- if \(x < 1\)

  $$\mu = \frac{R^2}{8} \left\{ \frac{1}{D_1} (1 - \ln A_2) + \frac{1}{D_2} (1 - x^2 - \ln A_1) - \frac{1}{D_2} \left( (1 + x^2 + w)^2 - 4x^2 \right)^{1/2} \right\}$$  \hspace{1cm} (29)

- if \(x > 1\)

  $$\mu = \frac{R^2}{8} \left\{ \frac{1}{D_1} (1 - \ln(A_2) + \frac{1}{D_2} (x^2 - 1 - \ln(x^4 A_1)) - \frac{1}{D_2} \left( (1 + x^2 + w)^2 - 4x^2 \right)^{1/2} \right\}$$  \hspace{1cm} (30)
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where

\[ A_1 = \frac{1}{2x^4} \left\{ (1 + x^2 + w)^2 - 2x^2 - (1 + x^2 + w)\sqrt{(1 + x^2 + w)^2 - 4x^2} \right\} \] (31)

and

\[ A_2 = \frac{1}{2x^4} \left\{ (1 - x^2 + w)^2 + 2wx^2 - (1 - x^2 + w)\sqrt{(1 + x^2 + w)^2 - 4x^2} \right\} \] (32)

In the special case when the two particles have the same diffusion coefficient \( D_1 = D_2 = D \), this last expressions simplify in

\[ \mu = \frac{R^2}{8D} f(x), \] (33)

where

\[ f(x) = \begin{cases} 
2 - x^2 - \sqrt{x^4 + 4} + \ln \left( \frac{x^4 + 8 + 4\sqrt{x^4 + 4}}{x^4} \right) & x < 1 \\
1 < x 
\end{cases} \] (34)

In the spirit of formula (3), it is interesting to obtain the mean value of \( \mu \) with respect to the initial position of \( r_2 \). Assuming that the particle 2 is initially uniformly distributed in the disc \( D(0, R) \), we get

\[ \langle \mu \rangle = \frac{\int_0^R r_2^{(0)} \int_0^{2\pi} d\theta_2^{(0)} \mu(r_2^{(0)})}{\pi R^2} \]
\[ = \frac{R^2}{16} \left\{ \frac{1}{D_1} b_1 \left( \frac{D_2}{D_1} \right) + \frac{1}{D_2} b_2 \left( \frac{D_2}{D_1} \right) \right\} \] (35)

where

\[ b_1(x) = a(x) - x + 2 \ln \left( \frac{2(x + a(x))}{x(x + 2 - a(x))(-x + a(x))} \right) \]
\[ b_2(x) = -2a(x) + 2 \ln \left( \frac{2}{x^2 + 4x + 2 - (x + 2)a(x)} \right) \]
\[ a(x) = \sqrt{(x(4 + x))} \] (36)

In the case of equal diffusion coefficients, it is given by the very simple formula

\[ \langle \mu \rangle \approx 0.28 \frac{R^2}{D} \] (37)

In the limit \( D_1 \gg D_2 \), we obtain \( \langle \mu \rangle \sim \frac{R^2}{8D_1} \ln \left( \frac{D_1}{D_2} \right) \), this result admitting the same interpretation than the one given after Eq. (16).

5. Three dimensional situation

We now turn to the most challenging situation, that is the three dimensional case for arbitrary initial conditions.
Integrating first over $y$ in Eq. (5) and denoting for simplicity $r_1^{(0)} = v$ and $r_2^{(0)} = u$, we have

$$
\mu = \frac{1}{(16\pi^2 D_1 D_2)^{3/2}} \int \left( \prod_{i=1}^2 dr_i \int_0^\infty \frac{dS(r_i)}{\sum_{j=1}^2 \frac{||r_j-r_j^{(0)}||^2}{4D_j}} \right)
$$

$$
= \frac{(2\pi)^2}{(16\pi D_1 D_2)^{3/2}} \int_0^R dr_1 \int_0^R dr_2 \int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \frac{r_1^2 r_2^2 \sin \theta_1 \sin \theta_2}{(r_1^2 + v^2 - 2r_1 v \cos \theta_1) + \frac{1}{D_1} (r_2^2 + u^2 - 2r_2 u \cos \theta_2)^2}
$$

It turns out that all the integrations can be performed exactly, and $\mu$ can be expressed in terms of elementary functions of the initial distances $v$ and $u$ of particles 1 and 2 to the center of the catalytic site. These (rather lengthy) expressions are listed in the Appendix.

Averaging over the initial positions of particles (which are supposed to be uniformly distributed in the reactive zone), we find

$$
\langle \mu \rangle = \frac{(4\pi)^2}{(4\pi R^3/3)^2} \int_0^R dv \int_0^R du \mu(v, u)
$$

$$
= \frac{R^2}{20\pi} \left\{ \frac{1}{D_1} m \left( \frac{D_1}{D_2} \right) + \frac{1}{D_2} m \left( \frac{D_2}{D_1} \right) \right\}
$$

(39)

where

$$
m(x) = 2 - 10 \ln(1 + x) - 2 \ln(1 + x) x^{1/2} + 16 \arctan(\sqrt{x}) - \frac{7}{2} x^{1/2}
$$

(40)

Note that in the special case when one of the two particles, say 2, is immobile ($D_2 = 0$), following the Wilemski-Fixman [3, 4, 5] approach and Eq.(7), we obtain the expression

$$
k_D = \frac{5}{6} (4\pi D_1 R)
$$

(41)

given in the paper of Doi [4], which differs from the Smoluchowski constant only by the factor 5/6.

Note also that in the special case when the particle 2 is immobile and initially within the catalytic region, we recover the expressions given in [12] for the mean residence time of a single Brownian particle within a sphere.

6. Conclusion

We have computed the mean joint residence time of two particles in a sphere, for very general initial conditions. In particular, we have obtained in all cases the dependence of this residence time as a function of the diffusion coefficients of the two particles. Such results can be especially useful for describing kinetics of a bimolecular reaction activated by catalytic sites. For this reaction in three dimensions, the effective reaction rate actually involves the mean joint residence time of two reactive particles inside a region centered on a catalytic site. This mean time, being averaged over all initial
positions of the two reactive particles inside the reactive region, is explicitly given by Eq. 39. This is our main result, which appears as a generalization of the expression of the reaction constant given by Wilemski and Fixman for a bimolecular reaction.

7. Appendix : Expressions of \( \mu \) in three dimensions

Considering the expression 38 of \( \mu \), we integrate over angular variables and obtain:

\[
\int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \frac{r_1^2 r_2^2 \sin \theta_1 \sin \theta_2}{\left( \frac{D_1}{D_1^r} (r_1^2 + v^2 - 2r_1v \cos \theta_1) + \frac{1}{D_2} (r_2^2 + u^2 - 2r_2u \cos \theta_2) \right)^2} = \frac{D_1 D_2 r_1 r_2}{4uv}
\]

\[
\ln \left( \frac{(D_2 r_1^2 + v^2) + D_1 (r_1^2 + u^2) + 2D_2 vr_1 - 2D_1 ur_2) (D_2 r_2^2 + v^2) + D_1 (r_2^2 + u^2) - 2D_2 vr_1 + 2D_1 ur_2)}{(D_2 r_1^2 + v^2) + D_1 (r_1^2 + u^2) - 2D_2 vr_1 - 2D_1 ur_2) (D_2 r_2^2 + v^2) + D_1 (r_2^2 + u^2) + 2D_2 vr_1 + 2D_1 ur_2} \right)^{\theta(u,v;D_1,D_2)}
\]

(42)

Integrating next by parts over the radial variables \( r_1 \) and \( r_2 \), we finally find for initial positions \( v \) and \( u \)

\[
\mu(v,u) = -\frac{1}{96\pi uv} \left\{ 16 \frac{uvR^2}{D_1} + 16R^3 \left( \frac{u}{D_1} f(u,v;D_1,D_2) + \frac{v}{D_2} f(v,u;D_2,D_1) \right) + 
+ 8uv \left( \frac{v^2}{D_1} h(u,v;D_1,D_2) + \frac{u^2}{D_2} h(v,u;D_2,D_1) \right) + 24uvR^2 \left( \frac{1}{D_1^2} h(u,v;D_1,D_2) + \frac{1}{D_2^2} h(v,u;D_2,D_1) \right) + 
+ \left[ D_1^2 u^4 + D_2^2 v^4 - 6D_1 D_2 u^2 v^2 - 6R^2 (D_1^2 u^2 + D_2^2 v^2 - D_1 D_2 (u^2 + v^2)) - 3R^4 (D_1 + D_2)^2 \right] \psi(u,v;D_1,D_2) \right\} + \eta(u,v;D_1,D_2)
\]

(43)

where

\[
f(u,v;D_1,D_2) = \arctan \left( \sqrt{\frac{D_2}{D_1}} \frac{(R+v)}{(R-u)} \right) + \arctan \left( \sqrt{\frac{D_2}{D_1}} \frac{(R+v)}{(R+u)} \right) - 
- \arctan \left( \sqrt{\frac{D_2}{D_1}} \frac{(R-v)}{(R-u)} \right) - \arctan \left( \sqrt{\frac{D_2}{D_1}} \frac{(R-v)}{(R+u)} \right)
\]

(44)

\[
h(u,v;D_1,D_2) = \arctan \left( \sqrt{\frac{D_1}{D_2}} \frac{(R+u)}{(R-v)} \right) + \arctan \left( \sqrt{\frac{D_1}{D_2}} \frac{(R+u)}{(R+v)} \right) + 
+ \arctan \left( \sqrt{\frac{D_1}{D_2}} \frac{(R-u)}{(R-v)} \right) + \arctan \left( \sqrt{\frac{D_1}{D_2}} \frac{(R-u)}{(R+v)} \right)
\]

(45)

\[
\psi(u,v;D_1,D_2) = 
\ln \left( \frac{(D_1 + D_2)^2 R^2 + D_1 u^2 + D_2 v^2 - 2D_1 u R + 2D_2 v R)((D_1 + D_2)^2 R^2 + D_1 u^2 + D_2 v^2 + 2D_1 u R - 2D_2 v R)}{(D_1 + D_2)^2 R^2 + D_1 u^2 + D_2 v^2 - 2D_1 u R - 2D_2 v R)((D_1 + D_2)^2 R^2 + D_1 u^2 + D_2 v^2 + 2D_1 u R + 2D_2 v R)} \right)^{\theta(u,v;D_1,D_2)}
\]

(46)

\[
\theta(u,v;D_1,D_2) = 
\ln \left( \frac{(D_1 + D_2)^2 R^2 + D_1 u^2 + D_2 v^2 - 2D_1 u R + 2D_2 v R)((D_1 + D_2)^2 R^2 + D_1 u^2 + D_2 v^2 + 2D_1 u R + 2D_2 v R)}{(D_1 + D_2)^2 R^2 + D_1 u^2 + D_2 v^2 + 2D_1 u R - 2D_2 v R)((D_1 + D_2)^2 R^2 + D_1 u^2 + D_2 v^2 - 2D_1 u R - 2D_2 v R)} \right)
\]

(47)
Mean joint residence time of two Brownian particles in a sphere

\[ \eta(u, v; D_1, D_2) = \begin{cases} 
1/2 R^2 \left( \frac{1}{D_1} + \frac{1}{D_2} \right) & u < R \text{ and } v < R \\
1/3 \frac{R^3}{u D_2} & R < u \text{ and } v < R \\
1/3 \frac{R^3}{v D_1} & u < R \text{ and } R < v \\
0 & \text{otherwise}
\end{cases} \]
Mean joint residence time of two Brownian particles in a sphere

[1] M. Smoluchowski, Z. Phys. Chem., 92 (1917) 129
[2] S. A. Rice, Diffusion-limited reactions, (Elsevier, Amsterdam, 1985)
[3] G. Wilemski and M. Fixman, J. Chem. Phys., 58, 4009 (1973)
[4] M. Doi, Chem. Phys., 11, 107 (1975)
[5] S. I. Temkin and B. I. Yakobson, J. Phys. Chem., 88, 2679 (1984)
[6] H. X. Zhou, J. Chem. Phys. 108, 8139 (1998)
[7] D. A. Darling and M. Kac, Trans. Am. Math. Soc. 84, 444 (1957)
[8] G. H. Weiss, Aspects and Applications of the Random Walk, (North-Holland, Amsterdam, 1994)
[9] A. Blumen and G. Zumofen, J. Chem Phys. 75, 892 (1981)
[10] G. Zumofen and A. Blumen, J. Chem Phys. 76, 3713 (1982)
[11] N. Agmon, J. Chem. Phys. 81, 3644 (1984)
[12] A. M. Berezhkovskii and V. Zaloj and N. Agmon, Phys. Rev. E 57, 3937 (2000)
[13] G. Kallianpur and H. Robbins, Proc. Nat. Acad. Sci. 39, 525 (1953)
[14] A. Bar-Haim and J. Klafter, J. Chem. Phys. 109, 5187 (1998)
[15] O. Bénichou, M. Coppey, J. Klafter, M. Moreau and G. Oshanin, Kinetics of diffusion-limited catalytically-activated reactions: An extension of the Wilemski-Fixman approach. To be submitted to J. Chem. Phys.
[16] O. Bénichou, M. Coppey, J. Klafter, M. Moreau and G. Oshanin, J. Phys A, 36, 7225 (2003)
[17] G. H. Weiss, J. Chem. Phys., 80, 2880 (1984)
[18] Gradshteyn and I. Ryzhik, Table of Integrals, Series and Products (Academic Press, New York, 1980)