

ON THE RADIAL MONOTONICITY OF THE ENSEMBLE AVERAGE  
PROPAGATOR

by

Erkam Bodur

B.S., Physics, Boğaziçi University, 2014

Submitted to the Institute for Graduate Studies in  
Science and Engineering in partial fulfillment of  
the requirements for the degree of  
Master of Science

Graduate Program in Physics

Boğaziçi University

2017

## ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to Assist. Prof. Evren Özarşlan of the Department of Biomedical Engineering at Linköping University for his continuous support of my master study with his immense knowledge. I would also like to thank my thesis advisor Prof. Mehmet Burçin Ünlü for his support and guidance.

I thank my fellow researcher mates Kadir and Serhat for their support and for all the fun we had in last few years. I would also thank my friends Muharrem and Ufuk for supporting me spiritually throughout writing my thesis.

My special thanks goes to my parents and to my brothers and sister for supporting me all my life.

I gratefully acknowledge the TÜBİTAK-2211 National Scholarship Programme for MSc Students.

**ABSTRACT****ON THE RADIAL MONOTONICITY OF THE ENSEMBLE  
AVERAGE PROPAGATOR**

The ensemble average propagator (EAP) is the diffusion propagator averaged over a volume of porous medium. This mathematical tool contains substantial amount of information concerning the geometry of the underlying structure. It is possible to measure the EAP via diffusion NMR methods which makes it relevant for many characterization studies. However, the mathematical properties of the EAP have not been fully studied and well-understood. In this thesis, we study the loss of radial monotonicity of the average propagator.

## ÖZET

### GURUP ORTALAMA YAYICISININ RADYAL TEKDÜZELİĞİ ÜZERİNE

Gurup ortalama yayıcısı difüzyon yayıcısının porlu ortamın hacmi üzerinden ortalaması alınarak elde edilir. Bu matematiksel araç ortamın geometrisi hakkında önemli derecede bilgi içerir. Ortalama yayıcının nükleer manyetik rezonans teknikleriyle ölçülebilir olması onu bir çok karakterlendirme çalışmasına ilişkili kılmaktadır. Buna rağmen matematiksel özellikleri tamamen çalışmış ve anlaşılmış değildir. Bu tezde ortalama yayıcının radyal tekdüzeliğinin kaybını çalıştım.

## TABLE OF CONTENTS

ACKNOWLEDGEMENTS . . . . .	iii
ABSTRACT . . . . .	iv
ÖZET . . . . .	v
LIST OF FIGURES . . . . .	viii
LIST OF SYMBOLS . . . . .	ix
LIST OF ACRONYMS/ABBREVIATIONS . . . . .	x
1. INTRODUCTION . . . . .	1
1.1. Random Walk 1-D . . . . .	2
1.2. 1-D Random Walk in the Presence of a Wall . . . . .	4
1.2.1. Reflecting Wall at $m = m_1$ . . . . .	4
1.2.2. Absorbing Wall at $m = m_1$ . . . . .	5
1.3. Generalization of the Problem: Markoff's Method . . . . .	6
1.3.1. Solution for Spherical Distribution of Displacement . . . . .	10
1.4. Diffusion Equation . . . . .	11
1.5. Diffusion Propagator . . . . .	13
2. RADIAL BEHAVIOR OF EAP FOR SHORT DIFFUSION TIMES . . . . .	17
2.1. Isotropic Environment . . . . .	17
2.1.1. No Collision, $r \rightarrow 0$ . . . . .	19
2.1.2. 1 Collision, $r \rightarrow 0$ . . . . .	20
2.1.3. No collision, $r \rightarrow r_a$ . . . . .	24
2.1.4. 1 Collision, $r \rightarrow r_a$ . . . . .	27
2.2. Anisotropic Environment . . . . .	30
2.2.1. No collision, $r \rightarrow 0$ . . . . .	33
2.2.2. 1 Collision, $r \rightarrow 0$ . . . . .	35
2.2.3. No collision, $r \rightarrow r_a$ . . . . .	39
2.2.4. 1 Collision, $r \rightarrow r_a$ . . . . .	43
2.3. Analysis for Monotonicity . . . . .	51
2.3.1. No Collision with Walls . . . . .	52
2.3.2. Effect of the Walls . . . . .	53

2.3.2.1. Isotropic EAP . . . . .	53
2.3.2.2. Anisotropic EAP . . . . .	53
3. RADIAL BEHAVIOR OF EAP FOR LONG DIFFUSION TIMES . . . . .	55
4. CONCLUSION . . . . .	57
REFERENCES . . . . .	59

## LIST OF FIGURES

Figure 2.1.	Angular average in Eq.(2.13) for a point near the wall. . . . .	21
Figure 3.1.	Considered pore shapes are illustrated on the top row, wherein white areas represent the fluid-filled pores. The corresponding long time EAPs are depicted in the second row after halving their size to be consistent with the upper figures. The EAP values along the center horizontal line are plotted on the bottom row. . . . .	56

## LIST OF SYMBOLS

$C_k^n$	Binomial coefficients for nonnegative $n$ and $k$
$D$	Diffusion constant
$G(m, N)$	Probability for a particle starting from origin to arrive at point $m$ after $N$ steps
$P$	Ensemble average propagator
$\mathcal{P}_l^m$	Legendre polynomial
$p_j$	Distribution of coordinates
$V_p$	Volume of porous medium
$\mathcal{Y}_l^m$	Spherical harmonics
$\delta_k$	Dirichlet integral
$\lambda_n$	Eigen values
$\Omega$	Solid angle
$\rho_s$	Surface relaxivity
$\Sigma$	Boundary surface
$u_n$	Eigen functions

## LIST OF ACRONYMS/ABBREVIATIONS

1D	One Dimensional
EAP	Ensemble Average Propagator
NMR	Nuclear Magnetic Resonance

## 1. INTRODUCTION

Diffusion is one of the earliest observed phenomenon in the history of physics. In ‘Nature of Things’ (60 BC), Lucretius states that the irregular motion of the dusty particles, revealing themselves under sunlight, is resulted from the random swerving of atoms. However, Robert Brown is the most famous scientist who is credited for the discovery of this phenomena. In 1827, while studying pollen grains under a microscope, he observed irregular motions of the particles in the water which has been referred as “Brownian Motion” afterwards. Albert Einstein, in 1905, put forward a solution to the problem while he was studying on the existence of atoms. His formulation successfully explains the Brownian motion which was later experimentally verified by Jean Baptiste Perrin in 1908.

Diffusion equation is probably one of the most studied equations in physics and material science due to both the phenomena itself and its direct relation to heat equation and Schrödinger equation. However, its mathematical properties are continuing to be discovered.

In the problem of determining the geometry of the boundaries and characterization of the porous media, diffusion propagator can be used as a probe [1,2]. Although diffusion propagator is very difficult to measure experimentally, its integration over a volume which is generally referred as “ensemble average propagator (EAP)” can be measured via NMR methods [3]. However, the mathematical properties of the EAP are not fully elucidated. Radial monotonicity would be one of the potentially useful property which has no rigorous proof yet. In this thesis, we studied the radial behavior of the EAP and look for the loss of radial monotonicity.

Before we start to our formulations regarding the radial behavior of the EAP, its plausible to give the derivation of the diffusion equation starting from 1D random walker problem. Historically, the problem clarified by famous scientists i.e. Lord Rayleigh, Karl Pearson [4–8]. We follow the methods given by Smoluchowski [9]

and R. von Mises [10] for the problem in the presence of reflecting and absorbing walls. In generalization process of random walk problem we used the Markoff method [8, 11, 12]. While transforming the the problem to diffusion equation we adopt the Chandrasekhar's [13] interpretation of the solution first given by Lord Rayleigh [14] then later by Smoluchowski [9].

### 1.1. Random Walk 1-D

Consider discrete movement of a particle along a straight line. At each step, the particle suffers an equal distance either backwards or forwards with an equal probability of 1/2. Let the particle begin its movement from the origin, then the probability for arriving to point  $m$  after  $N$  steps is given by

$$G(m, N) = (\# \text{ of distinct sequences of steps})(1/2)^N = \mathcal{C}_{(N+m)/2}^N (1/2)^N \quad (1.1)$$

where  $\mathcal{C}_k^n = \frac{n!}{(n-k)!k!}$ .

For our interest, look at the case when  $N \rightarrow \infty$  and  $m \ll N$  where

$$\begin{aligned} \log G(m, N) \approx & \left(N + \frac{1}{2}\right) \log N - \frac{1}{2}(N + m + 1) \log \left[\frac{N}{2} \left(1 + \frac{m}{2}\right)\right] \\ & - \frac{1}{2}(N - m + 1) \log \left[\frac{N}{2} \left(1 - \frac{m}{2}\right)\right] - \frac{1}{2} \log 2\pi - N \log 2 \end{aligned} \quad (1.2)$$

which is approximated by Stirling's formula as

$$\log a! = \left(a + \frac{1}{2}\right) \log a - a + \frac{1}{2} \log 2\pi + \mathcal{O}(n^{-1})(a \rightarrow \infty)$$

Since  $m \ll N$ , we have the series expansion

$$\log \left(1 \pm \frac{m}{N}\right) = \pm \frac{m}{N} - \frac{m^2}{2N^2} + \mathcal{O}(m^3/N^3)$$

Then, Eq.(1.2) becomes

$$\log G(m, N) \approx -\frac{1}{2} \log N + \log 2 - \frac{1}{2} \log 2\pi - \frac{m^2}{2N}$$

Thus for large  $N$ , the asymptotic formula for the probability is given as

$$G(m, N) = \left( \frac{2}{\pi N} \right)^{1/2} e^{-m^2/2N} \quad (1.3)$$

Let us introduce the net displacement  $x$  as a variable of  $G(x, N)$ .

$$x = ml \quad l: \text{ length of a step} \quad (1.4)$$

Since  $m$  can only be even or odd depending on whether  $N$  is odd or even, the probability  $G(x, N)\Delta x$  that the particle is happen to be in the interval  $(x, x + \Delta x)$  after  $N$  displacement is given by

$$G(x, N)\Delta x = G(m, N)(\Delta x/2l)$$

which gives

$$G(x, N) = \frac{1}{(2\pi Nl^2)^{1/2}} e^{-x^2/2Nl^2} \quad (1.5)$$

If the particle suffers  $n$  displacement per unit time, then the probability  $G(x, t)\Delta x$  that the particle arrives to the interval  $(x, x + \Delta x)$  after a time  $t$  is given by

$$G(x, t)\Delta x = \frac{1}{2(\pi Dt)^{1/2}} e^{-x^2/4Dt} \Delta x \quad (1.6)$$

where  $D = \frac{1}{2}nl^2$ .

## 1.2. 1-D Random Walk in the Presence of a Wall

It is convenient to examine 1-D random walk problem further in the cases of perfectly reflecting and absorbing barriers to understand the mathematical formulation of the diffusion process.

### 1.2.1. Reflecting Wall at $m = m_1$

In the presence of a perfectly reflecting wall at  $m = m_1 (m_1 > 0)$ , every particle reaching  $m_1$  has a probability unity to step back. Thus, every distinct sequence of steps that touching  $m_1$   $n$  times, should be counted  $2^n$  times. Reversing the sequences of steps preceding the the step that reaches to  $m_1$  gives another unique sequence that leads to  $2m_1 - m$  which is symmetric to  $m$  with respect to wall. If all the alternative unique sequences are counted for all reflections of reflected sequences as an addition to the counting of no-wall-case, we have the probability  $G(m, N; m_1)$  that a particle arrive to  $m$  after  $N$  steps in the presence of a reflecting wall at  $m = m_1$  given as

$$G(m, N; m_1) = G(m, N) + G(2m_1 - m, N) \quad (1.7)$$

For large  $N$ , Eq.(1.7) becomes

$$G(m, N; m_1) = \left( \frac{2}{\pi N} \right)^{1/2} [e^{-m^2/2N} + e^{-(2m_1-m)^2/2N}] \quad (1.8)$$

Then, we have the probability  $G(x, t; x_1)$  that particle end up between  $x$  and  $x + \Delta x$  after time  $t$  given as

$$G(x, t; x_1) = \frac{1}{2(\pi Dt)^{1/2}} [e^{-x^2/4Dt} + e^{-(2x_1-x)^2/4Dt}] \quad (1.9)$$

which satisfies

$$\left. \frac{\partial G}{\partial x} \right|_{x=x_1} = 0 \quad (1.10)$$

### 1.2.2. Absorbing Wall at $m = m_1$

Suppose that  $m_1 > 0$ , we look for the probability that particle reaches  $m$  after  $N$  steps. The presence of a perfectly absorbing wall at  $m = m_1$  means that the particle reaching to  $m_1$  has a zero probability to suffer further steps. With the same analogy we use in the case of reflecting wall, we count all the sequences which supposed to lead to image of  $m$  and exclude from the counting of the case of no walls. Finally, we have

$$G(m, N; m_1) = G(m, N) - G(2m_1 - m, N) \quad (1.11)$$

for the large  $N$ , it becomes

$$G(m, N; m_1) = \left( \frac{2}{\pi N} \right)^{1/2} [e^{-m^2/2N} - e^{-(2m_1-m)^2/2N}] \quad (1.12)$$

Then, we have

$$G(x, t; x_1) = \frac{1}{2(\pi Dt)^{1/2}} [e^{-x^2/4Dt} - e^{-(2x_1-x)^2/4Dt}] \quad (1.13)$$

Note that equ.(1.13) satisfies

$$G(x, t; x_1) = 0 \quad (1.14)$$

Another aspect of the problem reveals itself in calculating the probability  $H(m_1, N)$  that the particle arrives at  $m_1$  after  $N$  steps without ever touching  $m = m_1$  in an earlier step. After modifying the probability of the no-wall-case as we excluded the sequences that are prohibited in the case of the absorbing barrier, we have

$$H(m_1, N) = \frac{m_1}{N} \left( \frac{2}{\pi N} \right)^{1/2} e^{-m_1^2/2N} \quad (1.15)$$

which leads to the probability  $J(x, t)\Delta x$  that a particle arrives to  $x_1$  in the time interval  $(t, t + \Delta t)$  for the first time which is given by

$$J(x_1, t) = \frac{x_1}{t} \frac{1}{2(\pi Dt)^{1/2}} e^{x_1^2/4Dt} \quad (1.16)$$

Note that equ.(1.16) satisfies:

$$J(x_1, t) = -D \left( \frac{\partial G}{\partial x} \right) \Big|_{x=x_1} \quad (1.17)$$

Equ.(1.17) has crucial physical interpretations which we will refer in the section 1.4. Furthermore, note that Eq.(1.16) can be interpreted as the fraction of large number of particle initially concentrated at  $x = 0$  which are sedimented on the absorbing wall per unit time at time  $t$ .

### 1.3. Generalization of the Problem: Markoff's Method

After  $N$  displacements, the position of the particle is defined by

$$\vec{R} = \sum_{i=1}^N \vec{r}_i \quad (1.18)$$

where  $i$ 's are the different displacements. The probability that  $i$ th displacement lies between  $\vec{r}_i$  and  $\vec{r}_i + d\vec{r}_i$  is given by

$$p_i(x_i, y_i, z_i)dx_idy_idz_i = p_id\vec{r}_i \quad (i = 1, \dots, N) \quad (1.19)$$

Define a  $n$ -dimensional vector

$$\vec{\phi}_j = (\phi_j^1, \phi_j^2, \dots, \phi_j^n) \quad (j = 1, \dots, N) \quad (1.20)$$

whose components are function of  $q_j^i$ 's

$$\phi_j^k = \phi_j^k(q_j^1, \dots, q_j^s) \quad (k = 1, \dots, n; j = 1, \dots, N) \quad (1.21)$$

where  $s$ 's are the coordinates. The probability that  $q_j^s$  lies between

$$q_j^1, q_j^1 + dq_j^1; q_j^2, q_j^2 + dq_j^2; \dots; q_j^s, q_j^s + dq_j^s, \quad (j = 1, \dots, N)$$

defined as

$$p_j(q_j^1, \dots, q_j^s)dq_j^1 \dots dq_j^s = p_j(\vec{q}_j)d\vec{q}_j \quad (1.22)$$

Let us define the sum

$$(\Phi^1, \Phi^2, \dots, \Phi^n) = \vec{\Phi} = \sum_{j=1}^N \vec{\phi}_j \quad (1.23)$$

The probability that  $\vec{\Phi}_0 - (1/2)d\vec{\Phi}_0 \leq \vec{\Phi} \leq \vec{\Phi}_0 + (1/2)d\vec{\Phi}_0$ , where  $\vec{\Phi}_0$  is preassigned, is given by

$$G_N(\vec{\Phi}_0)d\vec{\Phi}_0^1 \dots d\vec{\Phi}_0^N = G(\vec{\Phi}_0)d\vec{\Phi}_0 = \int \dots \int \prod_{j=1}^N [p_j(\vec{q}_j)d\vec{q}_j] \quad (1.24)$$

Let us introduce  $\Delta(\vec{q}_1, \dots, \vec{q}_N)$  for this integral to be extended over whole configuration space.

$$\Delta(\vec{q}_1, \dots, \vec{q}_N) = \begin{cases} 1, & \text{if } \vec{\Phi}_0 - (1/2)d\vec{\Phi}_0 \leq \vec{\Phi} \leq \vec{\Phi}_0 + (1/2)d\vec{\Phi}_0 \\ 0, & \text{otherwise} \end{cases}$$

Consequently, we have:

$$G_N(\vec{\Phi}_0)d\vec{\Phi}_0 = \int \dots \int \Delta(\vec{q}_1, \dots, \vec{q}_N) \prod_{j=1}^N [p_j(\vec{q}_j)d\vec{q}_j] \quad (1.25)$$

The explicit expression for  $\Delta q$  can be given in Markoff's Method as a product of a Dirichlet integral. The integral is defined as

$$\delta_k = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\sin \alpha_k \rho_k}{\rho_k} e^{i\rho_k \gamma_k} d\rho_k \quad (k = 1, \dots, n) \quad (1.26)$$

which has the property

$$\delta_k = \begin{cases} 1, & \text{if } \alpha_k < \gamma_k < \alpha_k \\ 0, & \text{otherwise} \end{cases}$$

Then, using following substitutions

$$\alpha_k = \frac{1}{2}d\Phi_0^k; \quad \gamma_k = \sum_{j=1}^N \phi_j^k - \Phi_0^k \quad (k = 1, \dots, n) \quad (1.27)$$

we have

$$\delta_k = \begin{cases} 1, & \text{if } \Phi_0^k - (1/2)d\Phi_0^k < \sum_{j=1}^N \Phi_j^k < \Phi_0^k + (1/2)d\Phi_0^k \\ 0, & \text{otherwise} \end{cases}$$

Hence we have the explicit form for  $\Delta$  is given by

$$\Delta = \prod_{k=1}^n \delta_k \quad (1.28)$$

The probability in Eq.(1.25) becomes

$$\begin{aligned} G_N(\vec{\Phi}_0)d\vec{\Phi}_0 &= \frac{1}{\pi^n} \int \dots \int \int \dots \int \left[ \prod_{j=1}^N [p_i(\vec{q}_i) d\vec{q}_i] \right] \left[ \prod_{k=1}^n \frac{\sin((1/2)d\Phi_0^k \rho_k)}{\rho_k} \right] \\ &* \exp\left(i \left[ \sum_{k=1}^n \sum_{j=1}^N \phi_j^k \rho_k - \sum_{k=1}^n \Phi_0^k \rho_k \right]\right) d\rho_1 \dots d\rho_n \\ &= \frac{d\vec{\Phi}_0}{2^n \pi^n} \int \dots \int e^{-\vec{\rho} \cdot \vec{\Phi}_0} \mathcal{F}_N(\vec{\rho}) d\vec{\rho} \end{aligned} \quad (1.29)$$

where

$$\mathcal{F}_N(\vec{\rho}) = \prod_{j=1}^N \int \dots \int dq_j^1 \dots dq_j^s e^{i\vec{\rho} \cdot \vec{\phi}_j} p_i(q_j^1, \dots, q_j^s) \quad (1.30)$$

which becomes, for our interest, when all  $p_i$ 's are identical

$$\mathcal{F}_N(\vec{\rho}) = \left[ \int e^{i\vec{\rho} \cdot \vec{\phi}_j} p(\vec{q}) d\vec{q} \right]^N \quad (1.31)$$

Note that  $\mathcal{F}_N(\vec{\rho})$  is the n-dimensional Fourier transform of  $G(\vec{\Phi}_0)$ .

### 1.3.1. Solution for Spherical Distribution of Displacement

$G_N(\vec{R})d\vec{R}$  is the probability for the position of a particle to lie between  $\vec{R}$  and  $\vec{R} + d\vec{R}$  after  $N$  displacements

$$G_N(\vec{R}) = \frac{1}{8\pi^3} \int_{-\infty}^{+\infty} e^{-i\vec{\rho}\cdot\vec{R}} \mathcal{F}_N(\vec{\rho}) d\vec{\rho} \quad (1.32)$$

where

$$\mathcal{F}_N(\vec{\rho}) = \prod_{j=1}^N \int_{-\infty}^{+\infty} p_j(\vec{r}_j) e^{i\vec{\rho}\cdot\vec{r}_j} d\vec{r}_j \quad (1.33)$$

For the spherical distribution of displacement we have

$$p_j(\vec{r}_j) = p(|\vec{r}_j|^2), \quad (j = 1, \dots, N) \quad (1.34)$$

Thus, Eq.(1.33) takes the form

$$\begin{aligned} \mathcal{F}_N(\vec{\rho}) &= \left[ \int_{-\infty}^{+\infty} e^{i\vec{\rho}\cdot\vec{r}} p(r^2) d\vec{r} \right]^N \\ &= \left[ \int_0^\infty \int_0^\pi \int_0^{2\pi} e^{i|\vec{\rho}|r \cos\theta} r^2 p(r^2) d\omega d(-\cos\theta) dr \right]^N \\ &= \left[ 4\pi \int_0^\infty \frac{\sin(|\vec{\rho}|r)}{|\vec{\rho}|r} r^2 p(r^2) dr \right]^N \end{aligned} \quad (1.35)$$

For large  $N$  we have

$$\begin{aligned}
\lim_{N \rightarrow \infty} \mathcal{F}_N(\vec{\rho}) &= \lim_{N \rightarrow \infty} \left[ 4\pi \int_0^\infty \frac{\sin(|\vec{\rho}|r)}{|\vec{\rho}|r} r^2 p(r^2) dr \right]^N \\
&= \lim_{N \rightarrow \infty} \left[ 4\pi \int_0^{+\infty} \left( 1 - \frac{1}{6} |\vec{\rho}|^2 r^2 + \dots \right) r^2 p(r^2) dr \right]^N \\
&= e^{-N |\vec{\rho}|^2 \langle r^2 \rangle_{Av} / 6}
\end{aligned} \tag{1.36}$$

where  $\langle r^2 \rangle_{Av}$  is mean square displacement. By substituting (1.36) into (1.32), we have

$$\begin{aligned}
G_N(\vec{R}) &= \frac{1}{8\pi^3} \int_{-\infty}^{+\infty} e^{-i\vec{p} \cdot \vec{R} - N |\vec{\rho}|^2 \langle r^2 \rangle_{Av} / 6} d\vec{\rho} \\
&= \frac{1}{(2\pi N \langle r^2 \rangle_{Av} / 3)^{3/2}} e^{-3|\vec{R}|^2 / 2N \langle r^2 \rangle_{Av}}
\end{aligned} \tag{1.37}$$

#### 1.4. Diffusion Equation

Continuing from Eq.(1.37), the probability  $G(\vec{R})d\vec{R}$  that particle arrives to a volume element characterized by  $\vec{R}$  and  $\vec{R} + d\vec{R}$  after time  $t$  passes, where the distribution of displacement is spherical, is defined as

$$G(\vec{R})d\vec{R} = \frac{1}{(4\pi Dt)^{3/2}} e^{-|\vec{R}|^2 / 4Dt} d\vec{R} \tag{1.38}$$

where

$$D = n \langle r^2 \rangle_{Av} / 6 \tag{1.39}$$

Instead of using the large  $N$  limit to find an asymptotic solution, we can reach the same if we derive the corresponding differential equation. Results that are indicated in the problematization of 1D random walk, namely the vanishing values of  $G(x, t; x_1)|_{x=x_1}$  and  $(\partial G(x, t; x_1) / \partial x)|_{x=x_1}$  on absorbing and reflecting wall respectively, suggest such a differential equation.

Defining  $\Delta t$  such that the particle is able to suffer large number of steps at the same time  $\langle |\Delta \vec{R}|^2 \rangle_{Av}$  in  $\vec{R}$  stays small, we have the probability that the particle's displacement is  $\Delta \vec{R}$  in time interval  $\Delta t$

$$\mathcal{S}(\Delta \vec{R}; \Delta t) = \frac{1}{(4\pi D \Delta t)^{3/2}} e^{-|\Delta \vec{R}|^2 / 4D \Delta t} \quad (1.40)$$

Note that Eq.(1.40) is independent of  $\vec{R}$ . Thus we can express the probability distribution  $G(\vec{R}, t + \Delta t)$  at time  $t + \Delta t$  from distribution  $G(\vec{R}, t)$  at time  $t$

$$G(\vec{R}, t + \Delta t) = \int_{-\infty}^{+\infty} G(\vec{R} - \Delta \vec{R}, t) \mathcal{S}(\Delta \vec{R}; \Delta t) d(\Delta \vec{R}) \quad (1.41)$$

Taylor expansion of  $G(\vec{R}, t + \Delta t)$  for small  $\Delta \vec{R}$  is given by

$$\begin{aligned} G(\vec{R}, t + \Delta t) &= \frac{1}{(4\pi D \Delta t)^{3/2}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-|\Delta \vec{R}|^2 / 4D \Delta t} \left\{ G(\vec{R}, t) \right. \\ &\quad - \Delta X \frac{\partial W}{\partial X} - \Delta Y \frac{\partial W}{\partial Y} - \Delta Z \frac{\partial W}{\partial Z} + \frac{1}{2} \left[ + (\Delta X)^2 \frac{\partial^2 W}{\partial X^2} \right. \\ &\quad + (\Delta Y)^2 \frac{\partial^2 W}{\partial Y^2} + (\Delta Z)^2 \frac{\partial^2 W}{\partial Z^2} + 2\Delta X \Delta Y \frac{\partial^2 W}{\partial X \partial Y} \\ &\quad \left. \left. + 2\Delta Y \Delta Z \frac{\partial^2 W}{\partial Y \partial Z} + 2\Delta Z \Delta X \frac{\partial^2 W}{\partial Z \partial X} \right] + \dots \right\} d(\Delta X) d(\Delta Y) d(\Delta Z) \\ &= G(\vec{R}, t) + D \Delta t \left( \frac{\partial^2 G}{\partial X^2} + \frac{\partial^2 G}{\partial Y^2} + \frac{\partial^2 G}{\partial Z^2} \right) + \mathcal{O}([\Delta t]^2) \end{aligned} \quad (1.42)$$

Consequently we have

$$\frac{\partial G}{\partial t} \Delta t + \mathcal{O}([\Delta t]^2) = D \Delta t \left( \frac{\partial^2 G}{\partial X^2} + \frac{\partial^2 G}{\partial Y^2} + \frac{\partial^2 G}{\partial Z^2} \right) + \mathcal{O}([\Delta t]^2) \quad (1.43)$$

Then, for the limit  $\Delta t \rightarrow 0$  we have

$$\frac{\partial G}{\partial t} = D \left( \frac{\partial^2 G}{\partial X^2} + \frac{\partial^2 G}{\partial Y^2} + \frac{\partial^2 G}{\partial Z^2} \right) \quad (1.44)$$

which is the required differential equation of diffusion equation. Note that the probabilities we have concerned is about a particle arriving a volume element after some time passes. However, they can be interpreted as fraction of a large number of particles, that are initially concentrated at the origin, finding themselves in that volume element. In this interpretation  $G(\vec{R}, t)$  would be the concentration of diffusing particles at  $\vec{R}$  at time  $t$ . Thus, the amount of particle crossing an area  $\Delta\sigma$  in the time interval  $\Delta t$  is given by

$$-D(\hat{k} \cdot \nabla G)\Delta\sigma\Delta t \quad (\hat{k} \perp \Delta\sigma) \quad (1.45)$$

which indicates that the absorption rate of the particles per unit time per unit area in the presence of a perfectly absorbing barrier is expressed by

$$-D(\hat{k} \cdot \nabla G)_{G=0} \quad (1.46)$$

Note that Eq.(1.46) is in perfect agreement with Eq.(1.17).

### 1.5. Diffusion Propagator

The propagator  $G(\vec{r}_1, \vec{r}_2, t)$  represents the probability that a particle starting from the position  $\vec{r}_1$  travels to  $\vec{r}_2$  in time  $t$ .  $G(\vec{r}_1, \vec{r}_2, t)$  satisfies diffusion equation with following initial condition

$$\frac{\partial G(\vec{r}_1, \vec{r}_2, t)}{\partial t} = D\nabla^2 G(\vec{r}_1, \vec{r}_2, t), \quad \lim_{t \rightarrow 0} G(\vec{r}_1, \vec{r}_2, t) = \delta(\vec{r}_2 - \vec{r}_1) \quad (1.47)$$

and the boundary condition which is given as

$$\rho_s G(\vec{r}_1, \vec{r}_2, t) + D \hat{n} \cdot \nabla G(\vec{r}_1, \vec{r}_2, t) = 0, \quad \vec{r}_1 \in \Sigma \quad (1.48)$$

where  $\rho_s$  is the surface relaxivity. Eq.(1.48) is the generalized robin boundary condition which indicates that  $G(\vec{r}_1, \vec{r}_2, t)$  fully describes the diffusional motion for complex environments too. As Eq.(1.38) suggests, for a free diffusion in an isotropic environment, the propagator is given by

$$G(\vec{r}_1, \vec{r}_2; t) = \frac{1}{(4\pi Dt)^{3/2}} e^{-|\vec{r}_2 - \vec{r}_1|^2 / 4Dt} \quad (1.49)$$

In the presence of perfect reflecting wall at  $z = 0$ , we have the following system of equation with a Neumann boundary condition

$$\frac{\partial G(\vec{r}_1, \vec{r}_2, t)}{\partial t} = D \nabla G(\vec{r}_1, \vec{r}_2, t), \quad \lim_{t \rightarrow 0} G(\vec{r}_1, \vec{r}_2, t) = \delta(\vec{r}_2 - \vec{r}_1)$$

$$D \hat{n} \cdot \nabla G(\vec{r}_1, \vec{r}_2, t) = 0, \quad \vec{r}_1 \in \Sigma \quad (1.50)$$

Near the wall, the propagator is given by a free Gaussian and its image:

$$G(\vec{r}_1, \vec{r}_2; t) = \frac{1}{(4\pi Dt)^{3/2}} e^{-|x_2 - x_1|^2 / 4Dt} e^{-|y_2 - y_1|^2 / 4Dt} [e^{-|z_2 - z_1|^2 / 4Dt} + e^{-|z_2 + z_1|^2 / 4Dt}] \quad (1.51)$$

For perfect absorbing wall at  $z = 0$  we have the Dirichlet boundary condition:

$$\rho_s G(\vec{r}_1, \vec{r}_2, t) = 0, \quad \vec{r}_1 \in \Sigma \quad (1.52)$$

Thus, the solution is given by

$$G(\vec{r}_1, \vec{r}_2; t) = \frac{1}{(4\pi Dt)^{3/2}} e^{-|x_2-x_1|^2/4Dt} e^{-|y_2-y_1|^2/4Dt} [e^{-|z_2-z_1|^2/4Dt} - e^{-|z_2+z_1|^2/4Dt}] \quad (1.53)$$

Although  $G(\vec{r}_1, \vec{r}_2; t)$  is extremely powerful mathematical tool, it is very difficult to measure experimentally. However, the “ensemble average propagator (EAP)” which represent the overall probability that the particles suffer net displacement  $\vec{r}$  in time  $t$  which is given by

$$P_t(\vec{r}) = \int_{V_p} G(\vec{r}_1, \vec{r}_1 + \vec{r}; t) d^3r_1 \quad (1.54)$$

can be measured for instance via NMR methods. In the above expression,  $G(\vec{r}_1, \vec{r}_1 + \vec{r}; t)$  is a smooth function of  $r$  through the fluid and has a zero value within the solid construction of porous medium.

Implementation of the mathematical properties of EAP can enhance the numerical estimation EAP [15, 16]. An apparent property of EAP is that it has a positive value everywhere because it represents a probability for any finite volume. Although there are some exceptional conditions [17–19], another useful property of EAP is its antipodal symmetry

$$P_t(\vec{r}) = P_t(-\vec{r}) \quad (1.55)$$

which is a consequence of the reciprocity of the diffusion propagator which can be proven by using Green's theorem [20].

$$\begin{aligned}
& D \int_{t_1}^{t_2} dt \int_{V_p} dV [G(\vec{r}, \vec{r}_2; t_2 - t) \nabla^2 G(\vec{r}, \vec{r}_1; t - t_1) - G(\vec{r}, \vec{r}_1; t - t_1) \nabla^2 G(\vec{r}, \vec{r}_2; t_2 - t)] \\
&= \int_{V_p} dV \int_{t_1}^{t_2} dt \left[ G(\vec{r}, \vec{r}_2; t_2 - t) \frac{\partial G(\vec{r}, \vec{r}_1; t - t_1)}{\partial t} - G(\vec{r}, \vec{r}_1; t - t_1) \frac{\partial G(\vec{r}, \vec{r}_2; t_2 - t)}{\partial t} \right] \\
&= \int_{V_p} dV [G(\vec{r}, \vec{r}_1; t - t_1) G(\vec{r}, \vec{r}_2; t_2 - t)]_{t=t_1}^{t=t_2} \\
&= G(\vec{r}_2, \vec{r}_1; t_2 - t_1) - G(\vec{r}_1, \vec{r}_2; t_2 - t_1) = 0
\end{aligned} \tag{1.56}$$

Another potential property of the EAP is its radial monotonicity. However, no rigorous proof for this property has been suggested to our knowledge. In the following sections i try to give the detailed examination of radial behavior of the EAP.

## 2. RADIAL BEHAVIOR OF EAP FOR SHORT DIFFUSION TIMES

Reminding that  $G(\vec{r}_1, \vec{r}_2, t)$  is the conditional probability density that a walker released at  $\vec{r}_1$  at  $t = 0$  arrives to  $\vec{r}_2$  at  $t = t$  which satisfies the system of equation

$$\frac{\partial G(\vec{r}_1, \vec{r}_2, t)}{\partial t} = D\nabla G(\vec{r}_1, \vec{r}_2, t), \quad \lim_{t \rightarrow 0} G(\vec{r}_1, \vec{r}_2, t) = \delta(\vec{r}_2 - \vec{r}_1)$$

$$\rho_s G(\vec{r}_1, \vec{r}_2, t) + D\hat{n} \cdot \nabla G(\vec{r}_1, \vec{r}_2, t) = 0, \quad \vec{r}_1 \in \Sigma$$

The average propagator is defined as

$$P_t(\vec{r}) = \int d\vec{r}_1 G(\vec{r}_1, \vec{r}_2, t)$$

The examination of the radial behavior of the EAP is examined for the isotropic and anisotropic cases separately in the following sections

### 2.1. Isotropic Environment

For isotropic case, the EAP can be considered as averaged over solid angle

$$P_t(\vec{r}) = \frac{1}{4\pi} \int d\hat{\Omega} \int d\vec{r}_1 G(\vec{r}_1, \vec{r}_2, t) \tag{2.1}$$

Here, we look for whether the EAP shows radial monotonic decreasing or not. With the small  $\vec{r}$  expansion,  $\partial P_t(\vec{r})/\partial r$  is given by

$$\begin{aligned}
\frac{\partial P_t(\vec{r})}{\partial r} &= \frac{1}{4\pi} \int d\vec{r}_1 \int d\hat{\Omega} \frac{\partial G(\vec{r}_1, \vec{r}_2, t)}{\partial r} \\
&= \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\hat{\Omega} [G(\vec{r}_1, \vec{r}_2, t)|_{\vec{r}_2=\vec{r}_1} \\
&\quad + \vec{r} \cdot \vec{\nabla} G(\vec{r}_1, \vec{r}_2, t)|_{\vec{r}_2=\vec{r}_1} \\
&\quad + \frac{1}{2} \vec{r} \cdot [\vec{r} \cdot \vec{\nabla} (\vec{\nabla} G(\vec{r}_1, \vec{r}_2, t))]|_{\vec{r}_2=\vec{r}_1} + \dots] \\
&\approx \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\hat{\Omega} [G(\vec{r}_1, \vec{r}_1) + r_i \frac{\partial G(\vec{r}_1, \vec{r}_2)}{\partial r} |_{\vec{r}_2=\vec{r}_1} + \\
&\quad \frac{1}{2} r_i r_j \frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2) |_{\vec{r}_2=\vec{r}_1}]
\end{aligned} \tag{2.2}$$

Let us label the terms in the integral as follows:

$$T_1 = \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\hat{\Omega} G(\vec{r}_1, \vec{r}_1) \tag{2.3}$$

$$T_2 = \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\hat{\Omega} r_i \frac{\partial G(\vec{r}_1, \vec{r}_2)}{\partial r_i} |_{\vec{r}_2=\vec{r}_1} \tag{2.4}$$

$$T_3 = \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\hat{\Omega} \frac{1}{2} r_i r_j \frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2) |_{\vec{r}_2=\vec{r}_1} \tag{2.5}$$

In the following sections, we study the cases of no collision and 1-collision for both when  $\vec{r}$  goes to 0 and to arbitrary point  $\vec{r}_a$  within the pore.

### 2.1.1. No Collision, $r \rightarrow 0$

Since there is no boundary for this case,  $\partial P_t(\vec{r})/\partial r$  is given by

$$\frac{\partial P_t(\vec{r})}{\partial r} = \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta G(\vec{r}_1, \vec{r}_2; t) \quad (2.6)$$

Since  $\frac{\partial G(\vec{r}_1, \vec{r}_1)}{\partial r} = 0$ ,  $T_1$  is given by

$$T_1 = \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\hat{\Omega} G(\vec{r}_1, \vec{r}_1) = 0 \quad (2.7)$$

$T_2$  is given by

$$T_2 = \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta r_i \cdot \nabla_{r_{2i}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1} \quad (2.8)$$

where

$$\vec{r} = r(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$$

Let  $\hat{z}$  to be paralel to  $\nabla_{r_{2i}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1}$ , then we can write

$$\begin{aligned} T_2 &= \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\phi \int_0^\pi d\theta \sin \theta r \\ &(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \cdot (0, 0, |\nabla_{r_{2i}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1}|) \\ &\alpha \int_0^\pi d\theta \sin \theta \cos \theta = 0 \end{aligned} \quad (2.9)$$

For the  $T_3$  we have

$$T_3 = \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\hat{\Omega} \frac{1}{2} r_i r_j \frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2) \Big|_{\vec{r}_2 = \vec{r}_1} \propto \mathcal{O}(r) \quad (2.10)$$

Since we are interested in the limiting value  $r \rightarrow 0$

$$\lim_{r \rightarrow 0} T_3 = 0 \quad (2.11)$$

When  $r \rightarrow 0$ , if there is no collision with the wall, by summing up the results in Eq.(2.7), Eq.(2.9), Eq.(2.11),  $\partial P_t(\vec{r})/\partial r$  gives zero

$$\lim_{r \rightarrow 0} \frac{\partial P_t(\vec{r})}{\partial r} = \lim_{r \rightarrow 0} (T_1 + T_2 + T_3) = 0 \quad (2.12)$$

### 2.1.2. 1 Collision, $r \rightarrow 0$

For the case of 1 collision, imagine the sphere defined by the  $\vec{r}$ . The angular integration is restricted by the part of the sphere that does not intersect with the wall

$$\frac{\partial P_t(\vec{r})}{\partial r} = \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int_0^{2\pi} d\phi \int_\alpha^\pi d\theta \sin \theta G(\vec{r}_1, \vec{r}_2; t) \quad (2.13)$$

where  $\alpha$  is the angle  $\vec{r}$  makes with the normal of the wall as in Figure 2.1.

For  $T_1$ , we have

$$T_1 = \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int_0^{2\pi} d\phi \int_\alpha^\pi d\theta \sin \theta G(\vec{r}_1, \vec{r}_1) \quad (2.14)$$

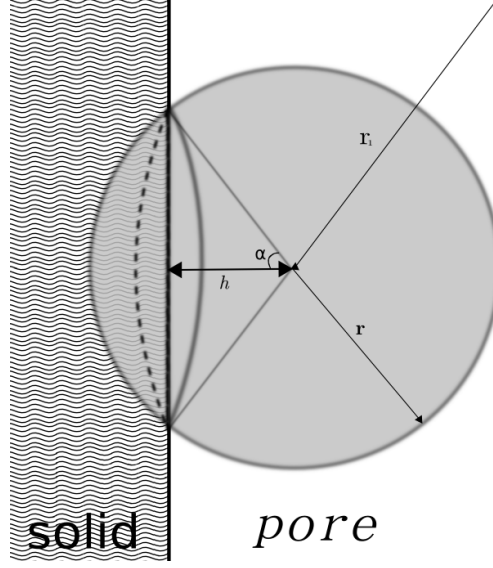


Figure 2.1. Angular average in Eq.(2.13) for a point near the wall.

The problem is assumed to be symmetric with respect to rotation about  $\hat{z}$  so  $\int_0^{2\pi} d\phi = 2\pi$ . The  $d\theta$  integral is given by

$$\int_{\alpha}^{\pi} d\theta \sin \theta = 1 + \frac{h}{r}$$

where  $h$  is the distance between  $r_1$  and the wall. Then Eq.(2.14) becomes

$$\begin{aligned} T_1 &= \frac{1}{2} \int d^2 r_s \int_0^r dh \frac{\partial}{\partial r} G(\vec{r}_1, \vec{r}_1) \left( 1 + \frac{h}{r} \right) \\ &= \frac{1}{2} \int d^2 r_s \int_0^r dh G(\vec{r}_1, \vec{r}_1) \left( \frac{-h}{r^2} \right) \end{aligned} \quad (2.15)$$

Let us expand  $G(\vec{r}_1, \vec{r}_1)$  for small  $h$

$$G(\vec{r}_1, \vec{r}_1) = G(h) = G(0) + h \left. \frac{\partial}{\partial z_1} G(h) \right|_{h=0} + \dots$$

where we choose  $z_1$  such that it is perpendicular to the wall. For the integration over the  $d\vec{r}_1$  in the boundary layer can be given as  $\int d^3 r_1 = \int d^2 r_s dh$ . Finally,  $T_1$  is given

by

$$\begin{aligned}
T_1 &= \frac{1}{2} \int d^2 r_s \int_0^r dh \left( G(0) + h \frac{\partial}{\partial z_1} G(h) \Big|_{h=0} \right) \left( \frac{-h}{r^2} \right) \\
&= \frac{1}{2} \int d^2 r_s \int_0^r dh (G(0)) \left( \frac{-h}{r^2} \right) + \frac{1}{2} \int d^2 r_s \int_0^r dh h \frac{\partial}{\partial z_1} G(h) \Big|_{h=0} \left( \frac{-h}{r^2} \right) \\
&= \frac{-1}{4} \int d^2 r_s G(\vec{r}_1, \vec{r}_1) \Big|_{\vec{r}_1 \in \Sigma} + \frac{-1}{6} r \int d^2 r_s \frac{\partial}{\partial z_1} G(h) \Big|_{h=0}
\end{aligned} \tag{2.16}$$

when  $r \rightarrow 0$ , the second term is vanished

$$\lim_{r \rightarrow 0} T_1 = \frac{-1}{4} \int d^2 r_s G(\vec{r}_1, \vec{r}_1) \Big|_{\vec{r}_1 \in \Sigma} \tag{2.17}$$

$T_2$  is given by

$$\begin{aligned}
T_2 &= \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int_0^{2\pi} d\phi \int_\alpha^\pi d\theta \sin \theta g(r(\sin \theta \cos \phi \sin \theta_g \cos \phi_g, \\
&\quad \sin \theta \sin \phi \sin \theta_g \sin \phi_g, \cos \theta \cos \theta_g))
\end{aligned} \tag{2.18}$$

where

$$\nabla_{r_{2i}} G(\vec{r}_1, \vec{r}_2) \Big|_{\vec{r}_2 = \vec{r}_1} = g(\sin \theta_g \cos \phi_g, \sin \theta_g \sin \phi_g, \cos \theta_g)$$

$$\vec{r} = r(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$$

Here,  $g$  expands around  $h = 0$  as

$$\begin{aligned}
g &= g(h) = g(0) + g'(0)h + \frac{1}{2}g''(0)h^2 + \dots \\
g'(h) &= \frac{\partial}{\partial z} g(h)
\end{aligned}$$

Note that  $\theta_g$  should be 0 where we choose  $\hat{z}$  to be parallel to normal of the wall, thus, we have

$$T_2 = \frac{2\pi}{4\pi} \int d^2r_s \int dh \frac{\partial}{\partial r} \int_{\alpha}^{\pi} \theta \sin \theta \cos \theta r g \quad (2.19)$$

where  $\int_{\alpha}^{\pi} d\theta \sin \theta \cos \theta = \frac{1}{2}(\frac{h^2}{r^2} - 1)$ .

Accordingly,  $T_2$  is given by

$$\begin{aligned} T_2 &= \frac{1}{4} \int d^2r_s \int_0^r dh \left( g(0) + g'(0)h + \frac{1}{2}g''(0)h^2 + \dots \right) \frac{\partial}{\partial r} r \left( \frac{h^2}{r^2} - 1 \right) \\ &= \frac{1}{4} \int d^2r_s \left[ \frac{-4rg(0)}{3} + \mathcal{O}(r^2) \right] \end{aligned} \quad (2.20)$$

for the limit  $r \rightarrow 0$ , we have

$$\lim_{r \rightarrow 0} T_2 = 0 \quad (2.21)$$

$T_3$  is given as

$$T_3 = \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\hat{\Omega} \frac{1}{2} r_i r_j \frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1} \alpha \mathcal{O}(r) \quad (2.22)$$

Thus, for the limit  $r \rightarrow 0$ ,  $T_3$  vanishes

$$\lim_{r \rightarrow 0} T_3 = 0 \quad (2.23)$$

Finally, for the 1-collision case, we have the sum of three terms in Eq.(2.17), Eq.(2.21) and Eq.(2.23) which is given as

$$\lim_{r \rightarrow 0} \frac{\partial P_t(\vec{r})}{\partial r} = \lim_{r \rightarrow 0} (T_1 + T_2 + T_3) = -\frac{1}{4} \int d^2 r_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma} \quad (2.24)$$

### 2.1.3. No collision, $r \rightarrow r_a$

Since the only difference is the limiting condition, for this section we have the same form for  $\partial P_t(\vec{r})/\partial r$  as in the Eq.(2.6)

$$\frac{\partial P_t(\vec{r})}{\partial r} = \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta G(\vec{r}_1, \vec{r}_2; t)$$

$T_1$  gives the same result as in  $r \rightarrow 0$  case

$$T_1 = \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\hat{\Omega} G(\vec{r}_1, \vec{r}_1) = 0 \quad (2.25)$$

since

$$\frac{\partial G(\vec{r}_1, \vec{r}_1)}{\partial r} = 0$$

$T_2$  also has the same result as in  $r \rightarrow 0$  case

$$T_2 = \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta r_i \cdot \nabla_{r_{2i}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2 = \vec{r}_1} \quad (2.26)$$

where

$$\vec{r} = r(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$$

Let  $\hat{z}$  to be paralel to  $\nabla_{r_{2i}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1}$ , then we can write

$$\begin{aligned}
T_2 &= \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\phi \int_0^\pi d\theta \sin \theta r \\
&\quad (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \cdot (0, 0, |\nabla_{r_{2i}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1}|) \\
&\propto \int_0^\pi d\theta \sin \theta \cos \theta = 0
\end{aligned} \tag{2.27}$$

$T_3$  is given by

$$T_3 = \frac{1}{8\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \mathcal{I} \tag{2.28}$$

where

$$\mathcal{I} = \int d\hat{\Omega} r_i r_j \frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1}$$

Choose the reference frame such that  $\frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1}$  is diagonalized. Define  $\vec{r}, r_2, M_{xx}, M_{yy}, M_{zz}$  as

$$\vec{r} = r(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$$

$$\vec{r}_2 = (x_2, y_2, z_2)$$

$$M_{xx} = \frac{\partial}{\partial r_{2x}} \frac{\partial}{\partial r_{2x}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1} = \frac{\partial^2 G}{\partial x_2^2} |_{x_2=x_1}$$

$$M_{yy} = \frac{\partial}{\partial r_{2y}} \frac{\partial}{\partial r_{2y}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1} = \frac{\partial^2 G}{\partial y_2^2}|_{y_2=y_1}$$

$$M_{zz} = \frac{\partial}{\partial r_{2z}} \frac{\partial}{\partial r_{2z}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1} = \frac{\partial^2 G}{\partial z_2^2}|_{z_2=z_1}$$

$$\begin{aligned} \mathcal{I} &= \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta [M_{xx} r^2 \sin^2 \theta \cos^2 \phi + M_{yy} r^2 \sin^2 \theta \sin^2 \phi + M_{zz} \cos^2 \theta] \\ &= 4\pi (M_{xx} + M_{yy} + M_{zz}) \frac{r^2}{3} \end{aligned} \quad (2.29)$$

By substituting Eq.(2.29) in to Eq.(2.28), and using the diffusion equation,  $T_3$  is finally given as

$$\begin{aligned} T_3 &= \frac{1}{8\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \frac{4r^2}{3} (M_{xx} + M_{yy} + M_{zz}) \\ &= \frac{r}{3} \int d\vec{r}_1 \text{Trace}(M)|_{r=R} \\ &= \frac{r}{3} \int d\vec{r}_1 \text{Trace}\left(\frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1}\right) \\ &= \frac{r}{3D} \frac{\partial}{\partial t} \int d\vec{r}_1 G(\vec{r}_1, \vec{r}_1) \end{aligned} \quad (2.30)$$

For the limit  $r \rightarrow r_a$  we can write

$$\lim_{r \rightarrow r_a} T_3 = \frac{r_a}{3D} \frac{\partial}{\partial t} \int d\vec{r}_1 G(\vec{r}_1, \vec{r}_1) \quad (2.31)$$

Hence, for the no collision case, when  $\vec{r} \rightarrow \vec{r}_a$ , the  $\partial P_t(\vec{r})/\partial r$  is resulted as

$$\lim_{r \rightarrow r_a} \frac{\partial P_t(\vec{r})}{\partial r} = \lim_{r \rightarrow r_a} (T_1 + T_2 + T_3) = \frac{r_a}{3D} \frac{\partial}{\partial t} \int d\vec{r}_1 G(\vec{r}_1, \vec{r}_1) \quad (2.32)$$

#### 2.1.4. 1 Collision, $r \rightarrow r_a$

We try to find the limiting value for

$$\frac{\partial P_t(\vec{r})}{\partial r} = \frac{1}{4\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \int_0^{2\pi} d\phi \int_\alpha^\pi d\theta \sin \theta G(\vec{r}_1, \vec{r}_2; t)$$

the calculation of  $T_1$  is the same in Eq.(2.16)

$$T_1 = \frac{-1}{4} \int d^2 r_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma} + \frac{-1}{6} r \int d^2 r_s \frac{\partial}{\partial z_1} G(h) \Big|_{h=0} \quad (2.33)$$

However, due to non-vanishing limit value for  $r$ , we still have the second term where the following substitution is possible

$$\frac{\partial}{\partial z_1} G(h)|_{h=0} = \frac{-\rho_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma}}{D}$$

where we used the boundary condition(1.48). Thus, when  $r \rightarrow r_a$ ,  $T_1$  is given by

$$\lim_{r \rightarrow r_a} T_1 = \frac{-1}{4} \int d^2 r_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma} + \frac{\rho_s r_a}{6D} \int d^2 r_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma} \quad (2.34)$$

$T_2$  is given by the Eq.(2.20)

$$T_2 = \frac{1}{4} \int d^2 r_s \left[ \frac{-4rg(0)}{3} + \mathcal{O}(r^2) \right]$$

Then, for the limit  $r \rightarrow r_a$ , it becomes

$$\lim_{r \rightarrow r_a} T_2 = -\frac{r_a}{3} \int d^2 r_s g(0) \quad (2.35)$$

By definition

$$g(0) = |\nabla G|_{\vec{r}_1 \in \Sigma}$$

which gives if we use the boundary condition(1.48)

$$g(0) = |\nabla G|_{\vec{r}_1 \in \Sigma} = \frac{-\rho_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma}}{D}$$

Hence, Eq.(2.35) could be written as

$$\lim_{r \rightarrow r_a} T_2 = \frac{\rho_s r_a}{3D} \int d^2 r_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma} \quad (2.36)$$

For the third term, we have

$$T_3 = \frac{1}{8\pi} \int d\vec{r}_1 \frac{\partial}{\partial r} \mathcal{I}_\alpha \quad (2.37)$$

where

$$\mathcal{I}_\alpha = \int d\hat{\Omega} r_i r_j \frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2 = \vec{r}_1}$$

Choose the reference frame such that  $\frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2 = \vec{r}_1}$  is diagonalized. Define  $\vec{r}, \vec{r}_2, M_{xx}, M_{yy}, M_{zz}$  as

$$\vec{r} = r(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$$

$$\vec{r}_2 = (x_2, y_2, z_2)$$

$$M_{xx} = \frac{\partial}{\partial r_{2x}} \frac{\partial}{\partial r_{2x}} G(\vec{r}_1, \vec{r}_2) |_{\vec{r}_2 = \vec{r}_1} = \frac{\partial^2 G}{\partial x_2^2} |_{x_2 = x_1}$$

$$M_{yy} = \frac{\partial}{\partial r_{2y}} \frac{\partial}{\partial r_{2y}} G(\vec{r}_1, \vec{r}_2) |_{\vec{r}_2 = \vec{r}_1} = \frac{\partial^2 G}{\partial y_2^2} |_{y_2 = y_1}$$

$$M_{zz} = \frac{\partial}{\partial r_{2z}} \frac{\partial}{\partial r_{2z}} G(\vec{r}_1, \vec{r}_2) |_{\vec{r}_2 = \vec{r}_1} = \frac{\partial^2 G}{\partial z_2^2} |_{z_2 = z_1}$$

$$\begin{aligned} \mathcal{I}_\alpha &= \int_0^{2\pi} d\phi \int_\alpha^\pi d\theta \sin \theta [M_{xx} r^2 \sin^2 \theta \cos^2 \phi + M_{yy} r^2 \sin^2 \theta \sin^2 \phi + M_{zz} \cos^2 \theta] \\ &= \pi r^2 \left( \frac{2}{3} + \frac{h}{r} + \frac{-h^3}{3r^2} \right) (M_{xx} + M_{yy}) + \pi r^2 \left( \frac{2}{3} - \frac{2h^3}{3r^3} M_{zz} \right) \end{aligned} \quad (2.38)$$

Then, we have

$$T_3 = \frac{1}{8} \int d^2 r_s \int dh \left[ \frac{4r}{3} (M_{xx} + M_{yy} + M_{zz}) + \left( h + \frac{h^3}{3r^2} (M_{xx} + M_{yy}) - \frac{2h^3}{3r^2} M_{zz} \right) \right] \quad (2.39)$$

Define  $Y_i$ 's as:

$$Y_1 = M_{xx} + M_{yy} + M_{zz}$$

$$Y_2 = (M_{xx} + M_{yy})$$

$$Y_3 = M_{zz}$$

$Y_i$  expands around  $h = 0$  as:

$$Y_i = Y_i(h) = Y_i(0) + hY_i'(0) + \dots$$

Accordingly, we get

$$\begin{aligned} T_3 = \frac{1}{8} \int d^2r_s \int_0^r dh & \left[ \frac{4r}{3} (Y_1(0) + hY_1'(0) + \dots) + \left( h + \frac{h^3}{3r^2} \right) (Y_2(0) + hY_2'(0) + \dots) \right. \\ & \left. - \frac{2h^3}{3r^2} (Y_3(0) + hY_3'(0) + \dots) \right] \end{aligned} \quad (2.40)$$

For the limit  $r \rightarrow r_a$ , we have

$$\begin{aligned} \lim_{r \rightarrow r_a} T_3 = \frac{1}{8} \int d^2r_s & \left[ \frac{4}{3} r_a^2 Y_1(0) + \mathcal{O}(r_a^3) + \frac{r_a^2}{2} Y_2(0) + \frac{r_a^2}{12} Y_2(0) + \mathcal{O}(r_a^2) \right. \\ & \left. - \frac{r_a^2}{6} Y_3(0) + \mathcal{O}(r_a^3) \right] \propto \mathcal{O}(r_a^2) \end{aligned} \quad (2.41)$$

For the 1-collision case, when  $r \rightarrow r_a$ ,  $\partial P_t(\vec{r})/\partial r$  is given by

$$\begin{aligned} \lim_{r \rightarrow r_a} \frac{\partial P_t(\vec{r})}{\partial r} &= \lim_{r \rightarrow r_a} (T_1 + T_2 + T_3) \\ &= \frac{-1}{4} \int d^2r_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma} + \frac{\rho_s r_a}{2D} \int d^2r_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma} \end{aligned} \quad (2.42)$$

## 2.2. Anisotropic Environment

We gave the calculations for the isotropic EAP which are resulted from spherical pores or random media which are the common case of interest. However, the environment revealing certain orientation leads to anisotropic EAP. We include the higher term in the spherical harmonic expansion of  $P_t(\vec{r})$  to account the anisotropy of the

environment.

$$P_t(r, \theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l a_{lm}(r) \mathcal{Y}_{lm}(\theta, \phi) \quad (2.43)$$

where

$$a_{lm} = \int_{S_r} P_t(r, \theta, \phi) \mathcal{Y}_{lm}^*(\theta, \phi) \sin \theta d\theta d\phi \quad (2.44)$$

whose radial difference gives the required coefficients in

$$\frac{\partial P_t(\vec{r})}{\partial r} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{\partial a_{lm}(r)}{\partial r} \mathcal{Y}_{lm}(\theta, \phi) \quad (2.45)$$

For this case too, we assume that the problem is symmetric around wall normal. Hence, other than  $\mathcal{Y}_n^0$  gives 0 due to  $\phi$  integral  $\int_0^{2\pi} d\phi \exp(i\phi m) = 0$ . Another cancellation comes from the reciprocity of  $G(\vec{r}_1, \vec{r}_2)$ :

$$G(\vec{r}_1, \vec{r}_2) = G(\vec{r}_2, \vec{r}_1)$$

which implies

$$P_t(\vec{r}) = P_t(-\vec{r})$$

so, only the spherical harmonics with the even  $l$  remains in the coefficients

$$\frac{\partial a_{l0}(r)}{\partial r} = \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\theta \mathcal{Y}_{l0}(\theta) G(\vec{r}_1, \vec{r}_2, t) \quad (2.46)$$

expanding for small  $r$

$$\begin{aligned} \frac{\partial a_{l0}(r)}{\partial r} &= \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\hat{\Omega} \mathcal{Y}_l^0 [G(\vec{r}_1, \vec{r}_1) + r_i \frac{\partial G(\vec{r}_1, \vec{r}_2)}{\partial r} \Big|_{\vec{r}_2=\vec{r}_1} \\ &\quad + \frac{1}{2} r_i r_j \frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2) \Big|_{\vec{r}_2=\vec{r}_1} + \dots] \end{aligned} \quad (2.47)$$

Let us label the terms as

$$T_1 = \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\hat{\Omega} \mathcal{Y}_l^0 G(\vec{r}_1, \vec{r}_1) \quad (2.48)$$

$$T_2 = \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\hat{\Omega} \mathcal{Y}_l^0 r_i \frac{\partial G(\vec{r}_1, \vec{r}_2)}{\partial r} \Big|_{\vec{r}_2=\vec{r}_1} \quad (2.49)$$

$$T_3 = \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\hat{\Omega} \mathcal{Y}_l^0 \frac{1}{2} r_i r_j \frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2) \Big|_{\vec{r}_2=\vec{r}_1} \quad (2.50)$$

The coefficients of the spherical harmonics  $\mathcal{Y}_l^0$  is given by

$$\mathcal{Y}_l^m = \sqrt{\frac{2l+1}{4\pi}} \sqrt{\frac{(l-m)!}{(l+m)!}} \mathcal{P}_l^m(\cos \theta)$$

$$\mathcal{Y}_l^0 = \sqrt{\frac{2l+1}{4\pi}} \mathcal{P}_l^0(\cos \theta)$$

$$\mathcal{P}_l^m(\cos \theta) = \frac{(-1)^m}{2^l l!} (1 - \cos^2 \theta)^{m/2} \frac{d^{l+m}}{d(\cos \theta)^{l+m}} (\cos^2 \theta - 1)^l$$

$$\begin{aligned} \mathcal{P}_l^0(\cos \theta) &= \frac{1}{2^l l!} \frac{d^l}{d(\cos \theta)^l} (\cos^2 \theta - 1)^l \\ \mathcal{Y}_l^0 &= \sqrt{\frac{2l+1}{4\pi}} \frac{1}{2^l l!} \frac{d^l}{d(\cos \theta)^l} (\cos^2 \theta - 1)^l \\ \mathcal{Y}_l^0 &= \sqrt{\frac{2l+1}{4\pi}} \frac{1}{2^l l!} \frac{d^l}{d(\cos \theta)^l} \sum_{p=0}^{p=l} \frac{l!}{(l-p)! p!} (\cos^2 \theta)^{l-p} (-1)^p \\ \mathcal{Y}_l^0 &= \sqrt{\frac{2l+1}{4\pi}} \frac{1}{2^l l!} \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(2l-2p-l)!} (\cos \theta)^{2l-2p-l} (-1)^p \end{aligned} \quad (2.51)$$

In the following sections, we study the cases of no collision and 1-collision for both when  $\vec{r}$  goes to 0 and to arbitrary point  $\vec{r}_a$  within the pore.

### 2.2.1. No collision, $r \rightarrow 0$

For this case, after calculating the terms of  $a_{l0}(r)$ , we will give the result for radial change of the EAP.

$T_1$  is given by

$$T_1 = \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\hat{\Omega} \mathcal{Y}_l^0 G(\vec{r}_1, \vec{r}_1)$$

where  $\frac{\partial G(\vec{r}_1, \vec{r}_1)}{\partial r} = 0$ , so we have

$$T_1 = 0 \quad (2.52)$$

$T_2$  is given by

$$T_2 = \int d\vec{r}_1 \frac{\partial}{\partial r} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \mathcal{Y}_n^0 \vec{r}_i \cdot \vec{\nabla}_{r_{2i}} G(\vec{r}_1, \vec{r}_2) |_{\vec{r}_2 = \vec{r}_1}$$

where

$$\vec{r} = r(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$$

Choose  $\hat{z}$  to be parallel to  $\vec{\nabla}_{r_{2i}} G(\vec{r}_1, \vec{r}_2) |_{\vec{r}_2 = \vec{r}_1}$ , then we get

$$T_2 = \int d\vec{r}_1 \frac{\partial}{\partial r} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \mathcal{Y}_n^0 |\nabla G| \cos \theta \propto \int_0^\pi d\theta \sin \theta \cos \theta \cos^n \theta \quad (2.53)$$

where

$$\int_0^\pi d\theta \sin \theta \cos \theta \cos^n \theta = \frac{-\cos^{n+2} \theta}{n+2} \Big|_0^\pi = \begin{cases} 0, & \text{if } n \text{ is even} \\ \frac{2}{n+2}, & \text{if } n \text{ is odd} \end{cases} \quad (2.54)$$

Since we interested only in  $\mathcal{Y}_l^0$  with even  $l$ ,

$$T_2 = 0 \quad (2.55)$$

$T_3$  is given by

$$T_3 = \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\hat{\Omega} \mathcal{Y}_n^0 \frac{1}{2} r_i r_j \frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2) |_{\vec{r}_2 = \vec{r}_1} \propto \mathcal{O}(r)$$

For the limit  $r \rightarrow 0$ , we have

$$\lim_{r \rightarrow 0} T_3 = 0 \quad (2.56)$$

Finally, for the no collision case with the limit  $r \rightarrow 0$ , the radial change of the EAP is given by

$$\lim_{r \rightarrow 0} \frac{\partial P_t(\vec{r})}{\partial r} = 0 \quad (2.57)$$

### 2.2.2. 1 Collision, $r \rightarrow 0$

For this case  $T_1$  is given by

$$\begin{aligned} T_1 &= \int d\vec{r}_1 \frac{\partial}{\partial r} \int_0^{2\pi} d\phi \int_\alpha^\pi d\theta \sin \theta \mathcal{Y}_n^0 G(\vec{r}_1, \vec{r}_1) \quad (2.58) \\ &= 2\pi \int d\vec{r}_1 G(\vec{r}_1, \vec{r}_1) \frac{\partial}{\partial r} \mathcal{I} \end{aligned}$$

where

$$\mathcal{I} = \int_\alpha^\pi -d(\cos \theta) \mathcal{Y}_l^0 = C_0 \sum_{p=0}^{p=\lfloor l/2 \rfloor} A(l, p) \int_\alpha^\pi -d(\cos \theta) \cos^{l-2p} \theta$$

where

$$C_0 = (4\pi)^{\frac{1}{2}}$$

$$A(l, p) = \frac{\sqrt{2l+1}}{2^l l!} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(l-2p)!} (-1)^p$$

After doing the  $d\theta$  integral,  $T_1$  takes the form

$$\begin{aligned} T_1 &= 2\pi \int d\vec{r}_1 G(\vec{r}_1, \vec{r}_1) \frac{\partial}{\partial r} C_0 \sum_{p=0}^{p=\lfloor l/2 \rfloor} A(l, p) \frac{(-1)^{l-2p+2} + (h/r)^{l-2p+1}}{l-2p+1} \\ &= -2\pi \int d\vec{r}_1 G(\vec{r}_1, \vec{r}_1) C_0 \sum_{p=0}^{p=\lfloor l/2 \rfloor} A(l, p) h^{l-2p+1} r^{l-2p+2} \end{aligned}$$

Let us expand  $G(\vec{r}_1, \vec{r}_1)$  for small  $h$

$$G(\vec{r}_1, \vec{r}_1) = G(h) = G(0) + h \left. \frac{\partial}{\partial z_1} G(h) \right|_{h=0} + \dots$$

where we choose  $z_1$  such that it is perpendicular to the wall. For the integration over the  $d\vec{r}_1$  in the boundary layer can be given as  $\int d^3 r_1 = \int d^2 r_s dh$ . Finally,  $T_1$  is given by

$$T_1 = -2\pi C_0 \int d^2 r_s \int_0^r dh G(0) \sum_{p=0}^{p=\lfloor l/2 \rfloor} A(l, p) h^{l-2p+1} r^{l-2p+2} + \mathcal{O}(r)$$

Then, for the limit  $r \rightarrow 0$  we have

$$\begin{aligned} T_1 &= 2\pi \int d^2 r_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma} \sqrt{\frac{2l+1}{4\pi}} \frac{1}{2^l l!} \\ &\quad \times \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(l-2p)!} \frac{1}{l-2p+2} (-1)^{p+1} \end{aligned} \quad (2.59)$$

$T_2$  is given by

$$T_2 = \int d\vec{r}_1 \frac{\partial}{\partial r} \int_0^{2\pi} d\phi \int_\alpha^\pi d\theta \sin \theta \mathcal{Y}_l^0(\vec{r}_i) \cdot \nabla_{\vec{r}_2} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2 = \vec{r}_1}$$

where

$$\nabla_{r_{2i}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1} = g(\sin \theta_g \cos \phi_g, \sin \theta_g \sin \phi_g, \cos \theta_g)$$

$$\vec{r} = r(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$$

Here,  $g$  expands around  $h = 0$  as

$$g = g(h) = g(0) + g'(0)h + \frac{1}{2}g''(0)h^2 + \dots$$

where  $g'(h) = \frac{\partial}{\partial z}g(h)$

Note that  $\theta_g$  should be 0 where we choose  $\hat{z}$  to be parallel to normal of the wall, thus, we have

$$\begin{aligned} T_2 = 2\pi \int d\vec{r}_1 \frac{\partial}{\partial r} r (g(0) + g'(0)h + \frac{1}{2}g''(0)h^2 + \dots) \sqrt{\frac{2l+1}{4\pi}} \\ \frac{1}{2^l l!} \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(2l-2p-l)!} (-1)^p \int_{\alpha}^{\pi} d\theta \sin \theta \cos \theta \cos^{l-2p} \theta \end{aligned} \quad (2.60)$$

where

$$- \int_{\alpha}^{\pi} d\theta \sin \theta \cos \theta \cos^{l-2p} \theta = - \frac{\cos^{l-2p+2}}{l-2p+2} \Big|_{\alpha}^{\pi} = \frac{(-1)^{l-2p+3} + (h/r)^{l-2p+2}}{l-2p+2}$$

Thus, we have

$$\begin{aligned}
T_2 = r2\pi \int d^2r_s g(0) \sqrt{\frac{2l+1}{4\pi}} \frac{1}{2^l l!} \left[ (-1)^{l+1} \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(l-2p)!} \frac{1}{l-2p+2} (-1)^p \right. \\
\left. - \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(l-2p)!} \frac{l-2p+1}{(l-2p+2)(l-2p+3)} (-1)^p \right] + \mathcal{O}(r^2)
\end{aligned} \tag{2.61}$$

For the limit  $r \rightarrow 0$ ,  $T_2$  is given by

$$\lim_{r \rightarrow 0} T_2 = 0 \tag{2.62}$$

$T_3$  is given by

$$T_3 = \int d\vec{r}_1 \frac{\partial}{\partial r} \int_0^{2\pi} d\phi \int_\alpha^\pi d\theta \sin \theta \mathcal{Y}_n^0 \frac{1}{2} r_i r_j \frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2) |_{\vec{r}_2 = \vec{r}_1} \propto \mathcal{O}(r)$$

For the limit  $r \rightarrow 0$ ,  $T_3$  is given by

$$\lim_{r \rightarrow 0} T_3 = 0 \tag{2.63}$$

Finally, for the 1 collision case with the limit  $r \rightarrow 0$ , the radial change of the EAP is given by

$$\lim_{r \rightarrow 0} \frac{\partial P_t(\vec{r})}{\partial r} = - \int d^2r_s G(\vec{r}_1, \vec{r}_1) |_{\vec{r}_1 \in \Sigma} \sum_{l=0,2,\dots} \mathcal{P}_l(\cos \theta) C_l \tag{2.64}$$

where

$$C_l = \frac{(2l+1)}{2^{l+1}} \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{(2l-2p)!}{(l-2p)!(l-p)!p!} \frac{(-1)^p}{l-2p+2} \quad (2.65)$$

### 2.2.3. No collision, $r \rightarrow r_a$

$T_1$  is given by

$$T_1 = \int d\vec{r}_1 \frac{\partial}{\partial r} \int d\hat{\Omega} \mathcal{Y}_l^0 G(\vec{r}_1, \vec{r}_1)$$

where  $\frac{\partial G(\vec{r}_1, \vec{r}_1)}{\partial r} = 0$ , so we have

$$T_1 = 0 \quad (2.66)$$

$T_2$  is given by

$$T_2 = \int d\vec{r}_1 \frac{\partial}{\partial r} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \mathcal{Y}_n^0 \vec{r}_i \cdot \vec{\nabla}_{r_{2i}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1}$$

where

$$\vec{r} = r(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$$

Choose  $\hat{z}$  to be parallel to  $\vec{\nabla}_{r_{2i}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1}$ , then we get

$$T_2 = \int d\vec{r}_1 \frac{\partial}{\partial r} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \mathcal{Y}_n^0 r |\nabla G| \cos \theta \propto \int_0^\pi d\theta \sin \theta \cos \theta \cos^n \theta \quad (2.67)$$

where

$$\int_0^\pi d\theta \sin \theta \cos \theta \cos^n \theta = \frac{-\cos^{n+2} \theta}{n+2} \Big|_0^\pi = \begin{cases} 0, & \text{if } n \text{ is even} \\ \frac{2}{n+2}, & \text{if } n \text{ is odd} \end{cases} \quad (2.68)$$

Since we are interested only in  $\mathcal{Y}_l^0$  with even  $l$ ,

$$T_2 = 0 \quad (2.69)$$

$T_3$  is given by

$$T_3 = \int d\vec{r}_1 \frac{\partial}{\partial r} \mathcal{I}_0$$

where

$$\mathcal{I}_0 = \int d\hat{\Omega} \mathcal{Y}_n^0 r_i r_j \frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2) \Big|_{\vec{r}_2 = \vec{r}_1}$$

Choose the reference frame such that  $\frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2) \Big|_{\vec{r}_2 = \vec{r}_1}$  is diagonalized. Define  $\vec{r}, \vec{r}_2, M_{xx}, M_{yy}, M_{zz}$  as

$$\vec{r} = r(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$$

$$\vec{r}_2 = (x_2, y_2, z_2)$$

$$M_{xx} = \frac{\partial}{\partial r_{2x}} \frac{\partial}{\partial r_{2x}} G(\vec{r}_1, \vec{r}_2) \Big|_{\vec{r}_2 = \vec{r}_1} = \frac{\partial^2 G}{\partial x_2^2} \Big|_{x_2 = x_1}$$

$$M_{yy} = \frac{\partial}{\partial r_{2y}} \frac{\partial}{\partial r_{2y}} G(\vec{r}_1, \vec{r}_2) \Big|_{\vec{r}_2 = \vec{r}_1} = \frac{\partial^2 G}{\partial y_2^2} \Big|_{y_2 = y_1}$$

$$M_{zz} = \frac{\partial}{\partial r_{2z}} \frac{\partial}{\partial r_{2z}} G(\vec{r}_1, \vec{r}_2) \Big|_{\vec{r}_2 = \vec{r}_1} = \frac{\partial^2 G}{\partial z_2^2} \Big|_{z_2 = z_1}$$

Then we have

$$\begin{aligned} \mathcal{I}_0 &= \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \mathcal{Y}_n^0 [M_{xx} r^2 \sin^2 \theta \cos^2 \phi + M_{yy} r^2 \sin^2 \theta \sin^2 \phi + M_{zz} \cos^2 \theta] \\ &= M_{xx} r^2 \pi \mathcal{J} + M_{yy} r^2 \pi \mathcal{J} + 2M_{zz} r^2 \pi \mathcal{J}' \end{aligned} \quad (2.70)$$

where

$$\begin{aligned} \mathcal{J} &= \sum_{p=0}^{p=\lfloor l/2 \rfloor} D(l, p) \int_0^\pi d\theta \sin^3 \theta \cos^{l-2p} \theta \\ &= \sum_{p=0}^{p=\lfloor l/2 \rfloor} D(l, p) \left[ \frac{-\cos^{l-2p+1} \theta}{l-2p+1} \Big|_0^\pi + \frac{\cos^{l-2p+3} \theta}{l-2p+3} \Big|_0^\pi \right] \\ &= \sum_{p=0}^{p=\lfloor l/2 \rfloor} D(l, p) \times \begin{cases} \frac{2}{l-2p+1} - \frac{2}{l-2p+3}, & \text{if } l-2p \text{ is even} \\ 0, & \text{if } l-2p \text{ is odd} \end{cases} \end{aligned} \quad (2.71)$$

$$\begin{aligned} \mathcal{J} &= \sum_{p=0}^{p=\lfloor l/2 \rfloor} D(l, p) \int_0^\pi d\theta \sin \theta \cos^2 \theta \cos^n \theta = \sum_{p=0}^{p=\lfloor l/2 \rfloor} D(l, p) \left[ -\frac{\cos^{l-2p+3} \theta}{l-2p+3} \Big|_0^\pi \right] \\ &= \sum_{p=0}^{p=\lfloor l/2 \rfloor} D(l, p) \times \begin{cases} \frac{2}{l-2p+3}, & \text{if } l-2p \text{ is even} \\ 0, & \text{if } l-2p \text{ is odd} \end{cases} \end{aligned} \quad (2.72)$$

Here, coefficient  $D(l, p)$  is given by

$$D(l, p) = \sqrt{\frac{2l+1}{4\pi}} \frac{1}{2^l l!} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(l-2p)!}$$

finally,  $T_3$  is given by

$$\begin{aligned} T_3 &= \int d\vec{r}_1 \frac{\partial}{\partial r} \mathcal{I} = \int d\vec{r}_1 \frac{\partial}{\partial r} 2\pi (M_{xx} + M_{yy}) r^2 \sqrt{\frac{2l+1}{4\pi}} \frac{1}{2^l l!} \\ &\times \sum_{p=0}^{\lfloor l/2 \rfloor} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(l-2p)!} \left[ \frac{1}{l-2p+1} - \frac{1}{l-2p+3} \right] (-1)^p \\ &+ \int d\vec{r}_1 \frac{\partial}{\partial r} 4\pi M_{zz} r^2 \sqrt{\frac{2l+1}{4\pi}} \frac{1}{2^l l!} \sum_{p=0}^{\lfloor l/2 \rfloor} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(l-2p)!} \frac{1}{l-2p+3} (-1)^p \end{aligned} \quad (2.73)$$

For the limit  $r \rightarrow r_a$ , we have

$$\begin{aligned} \lim_{r \rightarrow r_a} T_3 &= \int d\vec{r}_1 (M_{xx} + M_{yy}) \sqrt{\pi} \frac{r_a \sqrt{2l+1}}{2^l} \\ &\times \sum_{p=0}^{\lfloor l/2 \rfloor} \frac{(2l-2p)! (-1)^p}{(l-2p)! (l-p)! p!} \left( \frac{1}{l-2p+1} - \frac{1}{l-2p+3} \right) \\ &+ \int d\vec{r}_1 (M_{zz}) \sqrt{\pi} \frac{2r_a \sqrt{2l+1}}{2^l} \sum_{p=0}^{\lfloor l/2 \rfloor} \frac{(2l-2p)! (-1)^p}{(l-2p)! (l-p)! p!} \frac{1}{l-2p+3} \end{aligned} \quad (2.74)$$

Finally, for the no collision case with the limit  $r \rightarrow r_a$ , the radial change of the EAP is given by

$$\begin{aligned} \lim_{r \rightarrow r_a} \frac{\partial P_t(\vec{r})}{\partial r} &= \int d\vec{r}_1 (M_{xx} + M_{yy}) \sum_l \mathcal{P}_l(\cos \theta) \frac{r_a}{2} \frac{2l+1}{2^l} \\ &\times \sum_{p=0}^{\lfloor l/2 \rfloor} \frac{(2l-2p)! (-1)^p}{(l-2p)! (l-p)! p!} \left( \frac{1}{l-2p+1} - \frac{1}{l-2p+3} \right) \\ &+ \int d\vec{r}_1 (M_{zz}) \sum_l \mathcal{P}_l(\cos \theta) r_a \frac{2l+1}{2^l} \sum_{p=0}^{\lfloor l/2 \rfloor} \frac{(2l-2p)! (-1)^p}{(l-2p)! (l-p)! p!} \frac{1}{l-2p+3} \end{aligned} \quad (2.75)$$

By using NumPy which is package for scientific computing with Python, we calculated the sums appear in the above expression.

$$\begin{aligned} & \sum_l \mathcal{P}_l(\cos \theta) \frac{2l+1}{2^l} \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{(2l-2p)!(-1)^p}{(l-2p)!(l-p)!p!} \left( \frac{1}{l-2p+1} - \frac{1}{l-2p+3} \right) \\ &= \frac{2}{3} \mathcal{P}_0(\cos \theta) - \frac{2}{3} \mathcal{P}_2(\cos \theta) \end{aligned}$$

$$\sum_l \mathcal{P}_l(\cos \theta) \frac{2l+1}{2^l} \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{(2l-2p)!(-1)^p}{(l-2p)!(l-p)!p!} \frac{1}{l-2p+3} = \frac{1}{3} \mathcal{P}_0(\cos \theta) + \frac{2}{3} \mathcal{P}_2(\cos \theta)$$

Because there is no interaction with the walls we can assume that  $M_{xx} = M_{yy} = M_{zz}$ , which leads

$$\begin{aligned} \lim_{r \rightarrow r_a} \frac{\partial P_t(\vec{r})}{\partial r} &= \frac{r_a}{3} \int d\vec{r}_1 \text{Trace}(M) \\ &= \frac{r_a}{3} \int d\vec{r}_1 \text{Trace} \left( \frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2) \Big|_{\vec{r}_2 = \vec{r}_1} \right) \\ &= \frac{r_a}{3D} \frac{\partial}{\partial t} \int d\vec{r}_1 G(\vec{r}_1, \vec{r}_1) \end{aligned} \quad (2.76)$$

where we used the relation  $\mathcal{P}_0(\cos \theta) = 1$  and the diffusion equation in the last step. Note that the results for both isotropic and anisotropic environment is the same for the particles does not interact with the walls.

#### 2.2.4. 1 Collision, $r \rightarrow r_a$

For this case  $T_1$  is given by

$$T_1 = \int d\vec{r}_1 \frac{\partial}{\partial r} \int_0^{2\pi} d\phi \int_\alpha^\pi d\theta \sin \theta \mathcal{Y}_n^0 G(\vec{r}_1, \vec{r}_1) \quad (2.77)$$

$$= 2\pi \int d\vec{r}_1 G(\vec{r}_1, \vec{r}_1) \frac{\partial}{\partial r} \mathcal{I}$$

where

$$\mathcal{I} = \int_{\alpha}^{\pi} -d(\cos \theta) \mathcal{Y}_l^0 = C_0 \sum_{p=0}^{p=\lfloor l/2 \rfloor} A(l, p) \int_{\alpha}^{\pi} -d(\cos \theta) \cos^{l-2p} \theta \quad (2.78)$$

where

$$C_0 = (4\pi)^{\frac{1}{2}}$$

$$A(l, p) = \frac{\sqrt{2l+1}}{2^l l!} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(l-2p)!} (-1)^p$$

After doing the  $d\theta$  integral,  $T_1$  takes the form

$$\begin{aligned} T_1 &= 2\pi \int d\vec{r}_1 G(\vec{r}_1, \vec{r}_1) \frac{\partial}{\partial r} C_0 \sum_{p=0}^{p=\lfloor l/2 \rfloor} A(l, p) \frac{(-1)^{l-2p+2} + (h/r)^{l-2p+1}}{l-2p+1} \\ &= -2\pi \int d\vec{r}_1 G(\vec{r}_1, \vec{r}_1) C_0 \sum_{p=0}^{p=\lfloor l/2 \rfloor} A(l, p) h^{l-2p+1} r^{l-2p+2} \end{aligned}$$

Let us expand  $G(\vec{r}_1, \vec{r}_1)$  for small  $h$

$$G(\vec{r}_1, \vec{r}_1) = G(h) = G(0) + h \left. \frac{\partial}{\partial z_1} G(h) \right|_{h=0} + \dots$$

where we choose  $z_1$  such that it is perpendicular to the wall. For the integration over the  $d\vec{r}_1$  in the boundary layer can be given as  $\int d^3 r_1 = \int d^2 r_s dh$ . Finally,  $T_1$  is given

by

$$T_1 = -2\pi C_0 \int d^2 r_s \int_0^r dh (G(0) + h \frac{\partial}{\partial z_1} G(h)|_{h=0}) \sum_{p=0}^{p=\lfloor l/2 \rfloor} A(l, p) h^{l-2p+1} r^{l-2p+2} + \mathcal{O}(r^2)$$

$$T_1 = 2\pi \int d^2 r_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma} \sqrt{\frac{2l+1}{4\pi}} \frac{1}{2^l l!} \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(l-2p)!} \frac{1}{l-2p+2} (-1)^{p+1}$$

$$+ 2\pi r \int d^2 r_s \frac{\partial}{\partial z_1} G(h)|_{h=0} \sqrt{\frac{2l+1}{4\pi}} \frac{1}{2^l l!} \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(l-2p)!} \frac{1}{l-2p+3} (-1)^{p+1}$$

From boundary condition (1.48), we have:

$$\frac{\partial}{\partial z_1} G(h)|_{h=0} = \frac{-\rho_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma}}{D} \quad (2.79)$$

For the limit  $r \rightarrow r_a$ , we have

$$\begin{aligned} \lim_{r \rightarrow r_a} T_1 &= 2\pi \int d^2 r_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma} \sqrt{\frac{2l+1}{4\pi}} \frac{1}{2^l l!} \\ &\times \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(l-2p)!} \frac{1}{l-2p+2} (-1)^{p+1} \\ &- 2\pi \frac{r \rho_s}{D} \int d^2 r_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma} \sqrt{\frac{2l+1}{4\pi}} \frac{1}{2^l l!} \\ &\times \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(l-2p)!} \frac{1}{l-2p+3} (-1)^{p+1} \end{aligned} \quad (2.80)$$

$T_2$  is given by

$$T_2 = \int d\vec{r}_1 \frac{\partial}{\partial r} \int_0^{2\pi} d\phi \int_\alpha^\pi d\theta \sin \theta \mathcal{Y}_l^0 \vec{r}_i \cdot \nabla_{\vec{r}_{2i}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2 = \vec{r}_1}$$

where

$$\nabla_{r_{2i}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1} = g(\sin \theta_g \cos \phi_g, \sin \theta_g \sin \phi_g, \cos \theta_g)$$

$$\vec{r} = r(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$$

Here,  $g$  expands around  $h = 0$  as

$$g = g(h) = g(0) + g'(0)h + \frac{1}{2}g''(0)h^2 + \dots$$

where  $g'(h) = \frac{\partial}{\partial z}g(h)$

Note that  $\theta_g$  should be 0 where we choose  $\hat{z}$  to be parallel to normal of the wall, thus, we have

$$\begin{aligned} T_2 = 2\pi \int d\vec{r}_1 \frac{\partial}{\partial r} r (g(0) + g'(0)h + \frac{1}{2}g''(0)h^2 + \dots) \sqrt{\frac{2l+1}{4\pi}} \\ \frac{1}{2^l l!} \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(2l-2p-l)!} (-1)^p \int_{\alpha}^{\pi} d\theta \sin \theta \cos \theta \cos^{l-2p} \theta \end{aligned} \quad (2.81)$$

where

$$-\int_{\alpha}^{\pi} d\theta \sin \theta \cos \theta \cos^{l-2p} \theta = -\frac{\cos^{l-2p+2}}{l-2p+2} \Big|_{\alpha}^{\pi} = \frac{(-1)^{l-2p+3} + (h/r)^{l-2p+2}}{l-2p+2}$$

$$\begin{aligned} T_2 = B(l, p) \int d^2 r_s \int_0^r dh (g(0) + g'(0)h + \frac{1}{2}g''(0)h^2 + \dots) \\ \times \left( \frac{(-1)^{l-2p+3}}{l-2p+2} + \frac{l-2p+1}{l-2p+2} \left(\frac{h}{r}\right)^{l-2p+2} \right) \end{aligned} \quad (2.82)$$

where

$$B(l, p) = 2\pi \sqrt{\frac{2l+1}{4\pi}} \frac{1}{2^l l!} \sum_{p=0}^{\lfloor l/2 \rfloor} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(2l-2p-l)!} (-1)^p$$

$$T_2 = B(l, p) \int d^2 r_s \left[ \frac{r(-1)^{l-2p+1}}{l-2p+2} g(0) - \frac{r(l-2p+2)}{(l-2p+3)(l-2p+2)} g(0) \right] + \mathcal{O}(r^2)$$

By definition

$$g(0) = |\nabla G|_{\vec{r}_1 \in \Sigma}$$

which gives if we use the boundary condition(1.48)

$$g(0) = |\nabla G|_{\vec{r}_1 \in \Sigma} = \frac{-\rho_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma}}{D}$$

After neglecting terms with  $\mathcal{O}(r^2)$ , we have:

$$\begin{aligned} \lim_{r \rightarrow r_a} T_2 &= \frac{2\rho_s r_a}{D} \int d^2 r_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma} 2\pi \sqrt{\frac{2l+1}{4\pi}} \frac{1}{2^l l!} \\ &\times \sum_{p=0}^{\lfloor l/2 \rfloor} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(l-2p)!} \frac{(-1)^p}{l-2p+3} \end{aligned} \quad (2.83)$$

$T_3$  is given by

$$T_3 = \int d\vec{r}_1 \frac{\partial}{\partial r} \mathcal{I}_\alpha$$

where

$$\mathcal{I}_\alpha = \int_0^{2\pi} d\phi \int_\alpha^\pi d\theta \sin \theta \mathcal{Y}_n^0 \frac{1}{2} r_i r_j \frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2 = \vec{r}_1}$$

Choose the reference frame such that  $\frac{\partial}{\partial r_{2i}} \frac{\partial}{\partial r_{2j}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1}$  is diagonalized. Define  $\vec{r}, \vec{r}_2, M_{xx}, M_{yy}, M_{zz}$  as

$$\vec{r} = r(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$$

$$\vec{r}_2 = (x_2, y_2, z_2)$$

$$M_{xx} = \frac{\partial}{\partial r_{2x}} \frac{\partial}{\partial r_{2x}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1} = \frac{\partial^2 G}{\partial x_2^2}|_{x_2=x_1}$$

$$M_{yy} = \frac{\partial}{\partial r_{2y}} \frac{\partial}{\partial r_{2y}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1} = \frac{\partial^2 G}{\partial y_2^2}|_{y_2=y_1}$$

$$M_{zz} = \frac{\partial}{\partial r_{2z}} \frac{\partial}{\partial r_{2z}} G(\vec{r}_1, \vec{r}_2)|_{\vec{r}_2=\vec{r}_1} = \frac{\partial^2 G}{\partial z_2^2}|_{z_2=z_1}$$

Then we have

$$\begin{aligned} \mathcal{I}_\alpha &= \int_0^{2\pi} d\phi \int_\alpha^\pi d\theta \sin \theta \mathcal{Y}_n^0 [M_{xx} r^2 \sin^2 \theta \cos^2 \phi + M_{yy} r^2 \sin^2 \theta \sin^2 \phi + M_{zz} \cos^2 \theta] \\ &= M_{xx} r^2 \pi \mathcal{J} + M_{yy} r^2 \pi \mathcal{J} + 2M_{zz} r^2 \pi \mathcal{J}' \end{aligned} \tag{2.84}$$

where

$$\begin{aligned}
\mathcal{J} &= \sum_{p=0}^{p=\lfloor l/2 \rfloor} D(l, p) \int_{\alpha}^{\pi} d\theta \sin^3 \theta \cos^{l-2p} \theta \\
&= \sum_{p=0}^{p=\lfloor l/2 \rfloor} D(l, p) \left[ \frac{-\cos^{l-2p+1} \theta}{l-2p+1} \Big|_{\alpha}^{\pi} + \frac{\cos^{l-2p+3} \theta}{l-2p+3} \Big|_{\alpha}^{\pi} \right] \\
&= \sum_{p=0}^{p=\lfloor l/2 \rfloor} D(l, p) \frac{(-1)^{l-2p+2} + (h/r)^{l-2p+1}}{l-2p+1} + \frac{(-1)^{l-2p+4} + (h/r)^{l-2p+3}}{l-2p+3}
\end{aligned} \tag{2.85}$$

$$\begin{aligned}
\mathcal{J}' &= \sum_{p=0}^{p=\lfloor l/2 \rfloor} D(l, p) \int_{\alpha}^{\pi} d\theta \sin \theta \cos^2 \theta \cos^n \theta = \sum_{p=0}^{p=\lfloor l/2 \rfloor} D(l, p) \left[ -\frac{\cos^{l-2p+3}}{l-2p+3} \Big|_{\alpha}^{\pi} \right] \\
&= \sum_{p=0}^{p=\lfloor l/2 \rfloor} D(l, p) \frac{(-1)^{l-2p+4} + (h/r)^{l-2p+3}}{l-2p+3}
\end{aligned} \tag{2.86}$$

Here, coefficient  $D(l, p)$  is given by

$$D(l, p) = \sqrt{\frac{2l+1}{4\pi}} \frac{1}{2^l l!} \frac{l!}{(l-p)! p!} \frac{(2l-2p)!}{(l-2p)!}$$

consequently,  $\frac{\partial \mathcal{I}_{\alpha}}{\partial r}$  is given by

$$\begin{aligned}
\frac{\partial \mathcal{I}_{\alpha}}{\partial r} &= \pi K_1 \sum_{p=0}^{p=\lfloor l/2 \rfloor} D(l, p) \left[ \frac{2r(-1)^{l-2p+2}}{l-2p+1} + \frac{2r(-1)^{l-2p+4}}{l-2p+3} \right. \\
&\quad \left. - \frac{(l-2p-1)h^{l-2p+1}}{(l-2p+1)r^{l-2p-2}} + \frac{(l-2p+1)h^{l-2p+3}}{(l-2p+3)r^{l-2p+2}} \right] \\
&\quad + \pi K_2 \sum_{p=0}^{p=\lfloor l/2 \rfloor} D(l, p) \left[ \frac{2r(-1)^{l-2p+4}}{l-2p+3} + \frac{(l-2p+1)h^{l-2p+3}}{(l-2p+3)r^{l-2p+2}} \right]
\end{aligned} \tag{2.87}$$

where

$$K_1 = M_{xx} + M_{yy}, \quad K_2 = M_{zz}$$

whose expansion for small  $h$  is given by

$$K_1 = K_1(h) = K_1(0) + K_1'(0) + \dots, \quad K_2 = K_2(h) = K_2(0) + K_2'(0) + \dots$$

Finally,  $T_3$  is given by

$$\begin{aligned} T_3 &= \int dr_s^2 \int_0^r dh \pi (K_1(0) + K_1'(0) + \dots) \\ &\times \sum_{p=0}^{p=\lfloor l/2 \rfloor} D(l, p) \left[ \frac{2r(-1)^{l-2p+2}}{l-2p+1} + \frac{2r(-1)^{l-2p+4}}{l-2p+3} \right. \\ &\quad \left. - \frac{(l-2p-1)h^{l-2p+1}}{(l-2p+1)r^{l-2p-2}} + \frac{(l-2p+1)h^{l-2p+3}}{(l-2p+3)r^{l-2p+2}} \right] \\ &+ \int dr_s^2 \int_0^r dh \pi (K_2(0) + K_2'(0) + \dots) \\ &\times \sum_{p=0}^{p=\lfloor l/2 \rfloor} D(l, p) \left[ \frac{2r(-1)^{l-2p+4}}{l-2p+3} + \frac{(l-2p+1)h^{l-2p+3}}{(l-2p+3)r^{l-2p+2}} \right] \alpha \mathcal{O}(r^2) \end{aligned} \quad (2.88)$$

Finally, for the 1-collision case with the limit  $r \rightarrow r_a$ , the radial change of the EAP is given by

$$\begin{aligned} \lim_{r \rightarrow r_a} \frac{\partial P_l(\vec{r})}{\partial r} &= \int d^2 r_s G(\vec{r}_1, \vec{r}_1) |_{\vec{r}_1 \in \Sigma} \sum_l \mathcal{P}_l(\cos \theta) \frac{2l+1}{2^{l+1}} \\ &\times \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{(2l-2p)!}{(l-2p)!(l-p)!p!} \frac{(-1)^{p+1}}{l-2p+2} \\ &+ \int d^2 r_s G(\vec{r}_1, \vec{r}_1) |_{\vec{r}_1 \in \Sigma} \sum_l \mathcal{P}_l(\cos \theta) \frac{3\rho_s r_a}{2D} \frac{2l+1}{2^l} \\ &\times \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{1}{(l-p)!p!} \frac{(2l-2p)!}{(l-2p)!} \frac{(-1)^p}{l-2p+3} \end{aligned} \quad (2.89)$$

After numerical calculation by using NumPy, for the sum in the second term, we have:

$$\sum_l \mathcal{P}_l(\cos \theta) \frac{2l+1}{2^l} \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{1}{(l-p)!p!} \frac{(2l-2p)!}{(l-2p)!} \frac{(-1)^p}{l-2p+3} = \frac{1}{3} \mathcal{P}_0(\cos \theta) + \frac{2}{3} \mathcal{P}_2(\cos \theta)$$

where

$$\mathcal{P}_0(\cos \theta) = 1, \quad \mathcal{P}_2(\cos \theta) = \frac{1}{2}(3 \cos^2 \theta - 1)$$

Accordingly, we have

$$\lim_{r \rightarrow r_a} \frac{\partial P_t(\vec{r})}{\partial r} = \int d^2 r_s G(\vec{r}_1, \vec{r}_1) |_{\vec{r}_1 \in \Sigma} \left[ - \sum_{l=0,2,\dots} \mathcal{P}_l(\cos \theta) C_l + \frac{3\rho_s R \cos^2 \theta}{2D} \right] \quad (2.90)$$

where

$$C_l = \frac{(2l+1)}{2^{l+1}} \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{(2l-2p)!}{(l-2p)!(l-p)!p!} \frac{(-1)^p}{l-2p+2} \quad (2.91)$$

Note that as expected for  $l = 0$  Eq.(2.90) gives the result for isotropic case(2.42):

$$\frac{-1}{4} \int d^2 r_s G(\vec{r}_1, \vec{r}_1) |_{\vec{r}_1 \in \Sigma} + \frac{\rho_s r_a}{2D} \int d^2 r_s G(\vec{r}_1, \vec{r}_1) |_{\vec{r}_1 \in \Sigma}$$

### 2.3. Analysis for Monotonicity

In previous two sections, we gave the mathematical expression of the radial change of the EAP for both isotropic and anisotropic environments. Final results for either environment will be given by weighted sum of the expressions given in the no-collision and one-collision cases. In this section we look for whether the EAP reveals monotonic radial decay.

### 2.3.1. No Collision with Walls

As provided in the section 2.1.3. for isotropic environment and the section 2.2.3. for the anisotropic environment, when there is no wall, the radial change of the EAP at an arbitrary distance  $r_a$  is proportional to time derivative of the total return to origin probability which is given by the Eq.(2.32) and Eq.(2.76)

$$\frac{\partial P_t(\vec{r})}{\partial r} = \frac{r_a}{3D} \frac{\partial}{\partial t} \int dr_1 \vec{r}_1 G(\vec{r}_1, \vec{r}_1)$$

In the section 1.5, we define the diffusion propagator as the solution of the system of equations:

$$\frac{\partial G(\vec{r}_1, \vec{r}_2, t)}{\partial t} = D \nabla G(\vec{r}_1, \vec{r}_2, t), \quad \lim_{t \rightarrow 0} G(\vec{r}_1, \vec{r}_2, t) = \delta(\vec{r}_2 - \vec{r}_1)$$

$$\rho_s G(\vec{r}_1, \vec{r}_2, t) + D \hat{n} \cdot \nabla G(\vec{r}_1, \vec{r}_2, t) = 0, \quad \vec{r}_1 \in \Sigma$$

Note that the propagator can be given as eigen function expansion:

$$G(\vec{r}_1, \vec{r}_2; t) = \sum_{n=0}^{\infty} e^{-\lambda_n t} u_n(\vec{r}_1) u_n(\vec{r}_2)^* \quad (2.92)$$

where  $u_n(\vec{r})$  satisfies the equation

$$D \Delta u_n(\vec{r}) = -\lambda u_n(\vec{r}) \quad (2.93)$$

and the boundary condition

$$\rho_s u_n(\vec{r}) + D \hat{n} \cdot \nabla u_n(\vec{r}) = 0 \quad \vec{r} \in \Sigma \quad (2.94)$$

If we plug Eq.(2.92) in to Eq.(2.76), we have

$$\frac{\partial P_t(\vec{r})}{\partial r} = -\frac{r_a}{3D} \int_{V_p} \sum_{n=0}^{\infty} \lambda_n e^{-\lambda_n t} u_n(\vec{r}_1) u_n(\vec{r}_2)^* \quad (2.95)$$

where the long time behavior of the diffusion propagator requires all  $\lambda_n$  to be non-negative. Hence, the radial derivative of the EAP is negative everywhere except origin.

### 2.3.2. Effect of the Walls

When there are walls, the average fraction of particles interacts with the walls is  $S\sqrt{Dt}/V_p$ . In the sections 2.1.4. and 2.2.4., we provided the the solutions for the radial change of the EAP for the particles that suffers only one collision with a wall. Here, we analyze whether these solutions reveal monotonic behavior or not. Furthermore, note that final results for the EAP's are given by weighted sum of Eq.(2.76) and the results that are revisited in this section.

2.3.2.1. Isotropic EAP. For the isotropic case, the contribution to radial change of the EAP from the particles which suffers one collision with a wall is given by the Eq.(2.42)

$$\left( \frac{-1}{4} + \frac{\rho_s r_a}{2D} \right) \int d^2 r_s G(\vec{r}_1, \vec{r}_1) |_{\vec{r}_1 \in \Sigma}$$

which suggests that boundaries with small surface relaxivity result in monotonically decaying EAP.

2.3.2.2. Anisotropic EAP. As we shown in section 2.2.4., particles that undergoes one collision with a wall contributes the radial change of the anisotropic EAP ia given by the Eq.(2.90)

$$\left( - \sum_{l=0,2,\dots} \mathcal{P}_l(\cos \theta) C_l + \frac{3\rho_s r_a \cos^2 \theta}{2D} \right) \int d^2 r_s G(\vec{r}_1, \vec{r}_1) |_{\vec{r}_1 \in \Sigma}$$

where

$$C_l = \frac{(2l+1)}{2^{l+1}} \sum_{p=0}^{p=\lfloor l/2 \rfloor} \frac{(2l-2p)!}{(l-2p)!(l-p)!p!} \frac{(-1)^p}{l-2p+2}$$

The result we gave above could seem inconclusive because  $C_l$  is an alternating convergent series. However, we can approximate the summation very precisely for its extrema and infer the behavior in general. Results for  $\theta = 0$  and  $\theta = \pi/2$  are given respectively by

$$\approx \left( -\frac{1}{2} + \frac{3\rho_s r_a}{2D} \right) \int d^2 r_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma} \quad (2.96)$$

$$\approx -\frac{1}{12} \int d^2 r_s G(\vec{r}_1, \vec{r}_1)|_{\vec{r}_1 \in \Sigma} \quad (2.97)$$

Consequently, it is clear that the anisotropic EAP also reveals monotonic decay for small surface relaxivity.

### 3. RADIAL BEHAVIOR OF EAP FOR LONG DIFFUSION TIMES

We defined the average propagator as

$$P_t(\vec{r}) = \int_{V_p} G(\vec{r}_1, \vec{r}_1 + \vec{r}; t) d^3 r_1$$

where  $P_t$  vanishes within the solid construction of porous medium. If we introduce  $\rho_s(\vec{r})$  which represents the steady state density of particles,  $P_t(\vec{r})$  takes the form

$$P_t(\vec{r}) = \int_{V_p} \rho_s(\vec{r}_1) G(\vec{r}_1, \vec{r}_1 + \vec{r}; t) d^3 r_1 \quad (3.1)$$

where  $\rho_s(\vec{r}_1)$  is constant through the fluid filled medium and vanishes within the walls of the porous medium.

For the long diffusion times, the diffusion propagator becomes the indicator function, i.e.

$$\lim_{t \rightarrow \infty} G(\vec{r}_1, \vec{r}_2, t) = \rho_s(\vec{r}_2) \quad (3.2)$$

for closed systems. By substituting Eq.(3.2) in to Eq.(3.1), we have

$$P_t(\vec{r}) = \int_{V_p} \rho_s(\vec{r}_1) \rho_s(\vec{r}_1 + \vec{r}) d^3 r_1 \quad (3.3)$$

which is the autocorrelation of the pore indicator function. Hence, radial monotonicity is not a required property for the EAP in closed pores at long diffusion times.

The non-monotonicity of the EAP is illustrated in Figure 3.1 where we consider three different pores. On the top row, the white areas represents the fluid molecules and black ones is the pore structure. In the third geometry two media filled with fluid

separated by thin reflecting membrane.

On the middle row, the autocorrelation of the indicator functions are shown respectively. The EAP values along the center horizontal line are shown on the bottom row, which clearly indicate that monotonicity is not a general property of the EAP.

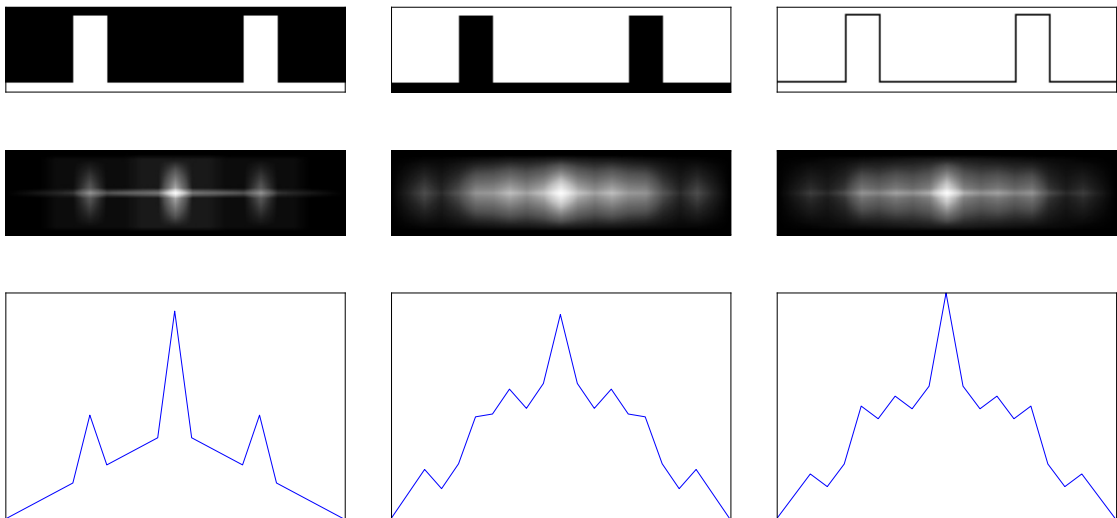


Figure 3.1. Considered pore shapes are illustrated on the top row, wherein white areas represent the fluid-filled pores. The corresponding long time EAPs are depicted in the second row after halving their size to be consistent with the upper figures. The EAP values along the center horizontal line are plotted on the bottom row.

By introducing a simple ansatz, Mitra et al. [1] showed that the diffusion propagator can be used as a probe to get structural data for connected systems. They suggested a modified Gaussian propagator which includes the pore-space correlation function. In this study, it is shown that the ansatz works well for probing the connectivity of periodic pore systems. Although our study did not include the monotonicity analysis for connected spaces in long time regime, the calculation we provided for the short time regime might be applicable to such [1] simple ansatz to study radial behavior of connected pore systems for future studies.

## 4. CONCLUSION

The diffusion propagator is studied extensively in characterization studies. Unlike the diffusion propagator, the EAP can be measured via NMR methods, which also contains great deal of information. Implementing the mathematical properties of the EAP improves the numerical estimation process of the EAP. We mainly focused on the radial behavior of the EAP.

For short diffusion times, our calculations show that radial change of the return to origin probability density immediately gives negative results by introducing the walls for both cases of isotropy and anisotropy.

In short time regime, we show that the particles that does not interact with the walls result in monotonically decaying EAP. However, the final results for the EAP are the weighted sum of the average propagators for no-collision case and 1-collision case. In section 2.3.2., we gave the contribution from the particles that collide only one times with the walls. It is clear that the boundaries introduce a possible non-monotonicity to radial change of the EAP. Nevertheless, the NMR measurements could provide much smoother version of the EAP we gave due to experimental dynamic of acquiring magnetization data.

Another mathematical property reveals itself is that for both isotropic and anisotropic environments whose boundaries' surface relaxivity is small enough, the EAP is always radially decaying function. This suggests that radial change of the EAP can be used as a physical constraint to enhance analysis of characterization of the pore structure.

For long diffusion times, the EAP becomes autocorrelation for pore indicator which states that radial monotonicity is not a general property for closed pores. Regarding connected system of pores, there is a study suggesting that diffusion propagator can probe certain properties of the structure with a simple ansatz introduced for long

time regime. For future studies, our calculations for short time regime seems applicable and modifiable for such ansatz to examine the radial behavior of the EAP for connected pores.

## REFERENCES

1. Mitra, P. P., P. N. Sen, L. M. Schwartz and P. Le Doussal, “Diffusion propagator as a probe of the structure of porous media”, *Physical review letters*, Vol. 68, No. 24, p. 3555, 1992.
2. Kac, M., “Can one hear the shape of a drum?”, *The american mathematical monthly*, Vol. 73, No. 4, pp. 1–23, 1966.
3. Stejskal, E., “Use of spin echoes in a pulsed magnetic-field gradient to study anisotropic, restricted diffusion and flow”, *The Journal of Chemical Physics*, Vol. 43, No. 10, pp. 3597–3603, 1965.
4. Rayleigh, L., “Xii. on the resultant of a large number of vibrations of the same pitch and of arbitrary phase”, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, Vol. 10, No. 60, pp. 73–78, 1880.
5. Pearson, K., “The problem of the random walk”, *Nature*, Vol. 72, No. 1865, p. 294, 1905.
6. Von Smoluchowski, M., “Zur kinetischen theorie der brownischen molekularbewegung und der suspensionen”, *Annalen der physik*, Vol. 326, No. 14, p. 203, 1906.
7. Kluyver, J., “Een vraagstuk van meetkundige waarschijnlijkheid”, *Koninklijke Akademie van Wetenschappen te Amsterdam. Wisen Natuurkundige Afdeling. Verslagen van de Gewone Vergaderingen*, Vol. 14, No. 1905-06, pp. 325–334, 1905.
8. Markov, A. A., *Wahrscheinlichkeits-rechnung*, Leipzig und Berlin, 1912.
9. Smoluchowski, M. v., “Zusammenfassende bearbeitungen”, *Phys. Z*, Vol. 17, pp. 557–559, 1916.

10. Mises, R. v., *Wahrscheinlichkeitsrechnung*, Leipzig und Wien, 1931.
11. Laue, M., “Ein Satz der Wahrscheinlichkeitsrechnung und seine Anwendung auf die Strahlungstheorie”, *Annalen der Physik*, Vol. 47, p. 853, 1915.
12. Rayleigh, L., “XXXI. On the problem of random vibrations, and of random flights in one, two, or three dimensions”, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, Vol. 37, No. 220, pp. 321–347, 1919.
13. Chandrasekhar, S., “Stochastic problems in physics and astronomy”, *Reviews of modern physics*, Vol. 15, No. 1, p. 1, 1943.
14. Lord, R., “On James Bernoulli’s theorems in probabilities”, *Phil. Mag*, Vol. 47, p. 246, 1899.
15. Özarıslan, E., C. G. Koay, T. M. Shepherd, M. E. Komlosh, M. O. İrfanođlu, C. Pierpaoli and P. J. Basser, “Mean apparent propagator (MAP) MRI: a novel diffusion imaging method for mapping tissue microstructure”, *NeuroImage*, Vol. 78, p. 16, 2013.
16. Paquette, M., G. Gilbert and M. Descoteaux, “Optimal DSI reconstruction parameter recommendations: Better ODFs and better connectivity”, *NeuroImage*, Vol. 142, p. 1, 2016.
17. Özarıslan, E., U. Nevo and P. J. Basser, “Anisotropy induced by macroscopic boundaries: surface-normal mapping using diffusion-weighted imaging”, *Biophysical journal*, Vol. 94, No. 7, 2008.
18. Liu, C., R. Bammer and M. E. Moseley, “Generalized Diffusion Tensor Imaging (GDTI): A Method for Characterizing and Imaging Diffusion Anisotropy Caused by Non-Gaussian Diffusion”, *Israel Journal of Chemistry*, Vol. 43, No. 1-2, p. 145, 2003.

19. Özarslan, E., C. G. Koay and P. J. Basser, “Remarks on q-space MR propagator in partially restricted, axially-symmetric, and isotropic environments”, *Magnetic resonance imaging*, Vol. 27, No. 6, p. 834, 2009.
20. Bergman, D. J. and K.-J. Dunn, “NMR of diffusing atoms in a periodic porous medium in the presence of a nonuniform magnetic field”, *Physical Review E*, Vol. 52, No. 6, p. 6516, 1995.