BACHELOR

Directionality of diffusion on curved surfaces
anisotropic diffusion on the surface of a cylinder in three dimensional simulations

van Leuken, S.H.M.

Award date:
2015

Link to publication
Directionality of diffusion on curved surfaces
Anisotropic diffusion on the surface of a cylinder in three dimensional simulations

Author: Stijn van Leuken
Supervisors/Guided by: Ir. R.P.T. Kusters Dr. W.G. Ellenbroek

July 11, 2015
Abstract

In this project we have studied the effect of curvature on the directionality of diffusion. For this, we measure the diffusion of spherical Lennard-Jones particles in the circumferential and longitudinal direction on the surface of a cylinder. As an improvement to earlier research with two dimensional simulations [3], we invoke three dimensional Langevin dynamics simulations, to account for the spherical shape of the particles. For radius of the cylinder a few times bigger than the radius of the particles or smaller, the circumferential component of the diffusion coefficient is larger than the longitudinal component. In comparison to the two dimensional simulations we reported a significant anisotropy in the diffusion coefficient, even at low surface densities. Moreover, our data suggested a non-monotonic dependence of the the amount of anisotropy on the density.
1 Introduction

In this project, the effect of curvature on the directionality of diffusion is researched. For this, the diffusion of particles in the circumferential and longitudinal direction on a cylinder are compared. The movement of particles can be described by a random walk. For interacting particles on a flat surfaces (neglecting other physics), the amount of diffusion is equal in all directions. For curved surfaces this is not necessarily true. The amount of diffusion in the direction with curvature can differ from the diffusion in a flat direction. This phenomenon is called anisotropic diffusion.

Knowledge about the directionality of diffusion can be of interest in biological systems. An example of such a biological system is a dendritic spine on a neuron. The surfaces of dendritic spines are partly covered with proteins that can diffuse over the surface. Many researches indicate the involvement of a specific type of protein, the so called glutamate receptor, in a learning process [1]. The relation between the diffusion of the receptors and the curvature (shape) of the dendritic spines can influence the density of receptors on the surface of the dendritic spines. A second way the knowledge about the directionality of diffusion can be used is for applications in the development of technology. An example of such applications is diffusion coating [2]. Curved surfaces could have the requirement that coating is equally distributed over their surface. The directionality of diffusion could influence this process.

The directionality of diffusion is already indicated by Kusters et al. [3]. They conducted two dimensional simulations using Langevin dynamics. To mimic the cylindrical surface, they used periodic rendered boundaries to create an unfolded cylinder. Their simulations indicate that in the case of a small circumference of the cylinder, particles diffuse more in the circumferential direction than in the longitudinal direction [3].

The goal of this project is to find the characteristics of diffusion on curved surfaces. One of the most simplified shapes of curved surfaces is a cylinder, because it contains one flat direction (the longitudinal direction) and one curved direction (the circumferential direction). In this project the directionality of diffusion on a cylinder is tested in a three dimensional simulations. This is a small step to a more realistic simulations in comparison with the two dimensional simulations. So the main research question is:

How does the curvature of a cylinder influence the actual diffusion in the longitudinal and circumferential direction?

This report starts with the theory behind Langevin dynamics and diffusion. Then the derivation of the surface density is discussed. Langevin dynamics are used to simulate the diffusion of the particles on the cylinders. The chapter "Setup", contains more information about the used simulation method. Also the method of processing and analysing the data and how the diffusion is determined from this are discussed in this section of the report.

In the chapter "Results and discussion", the findings and analysis of the simulations are discussed. We determine the minimal length of time steps where the dependency of the mean square displacement of the particles becomes linear. This information is used for the determination of the diffusion in the circumferential direction and the longitudinal direction. This is done for cylinders with varying radius. Also the influence of the surface density is investigated.

To find explanations for the found differences in the diffusion, the ordering of particles is researched. Besides this, we give an explanation of the cooperative movement of particles and the blocking of particles in the longitudinal direction due to the curvature. Throughout the analysis a comparison between the three dimensional simulations and two dimensional simulations is made. The report ends with an answer to the main research question and an advice for future research in the chapter "Conclusion and future research".
2 Theory

In this project we consider the diffusion of particles that move freely over the surface of a cylinder. To simulate this, we invoke Langevin dynamics. In the first section of this chapter the theory behind Langevin dynamics is discussed. In the second section some important concepts of diffusion that are used in this project are described. In the simulation, the particles are spheres and their middle points are forced to the surface of the cylinder. Due to the curvature of the cylinder, the shape of the surface of these particles on the cylinders is not exactly circular. In the third section the covered area of the particles on the cylinder is derived. In section four, we describe the Lennard-Jones potential. This potential is used for the interaction of the particles.

2.1 Langevin dynamics

The dynamics of colloidal particles at a microscopic scale is a complex many-body problem. The Langevin equation is an equation that describes the Brownian motion of these particles in a simplified way. The basic equation for Langevin dynamics is: \[ M \frac{dV}{dt} = -\zeta M V + F(R) + \Theta(t). \] (1)

In this equation, \( M \) is the mass, \( V \) and \( R \) are the particles velocity and position, \(-\zeta M V\) is the systematic contribution to the force (for example friction), \( F(R) \) describes the deterministic forces and \( \Theta \) the random force that represents the interaction of the particles with the fluid.

The random force depends on the configuration of the particles at microscopic scale. The fluctuation dissipation relation gives the connection between the fluctuating random force and the friction. This formula can be derived by taking the time average of the squared velocity described by the Langevin equation. The result is that \( \Theta(t) \) must satisfy
\[ \langle \Theta(t) \rangle = 0 \]
and
\[ \langle \Theta(t) \Theta(t') \rangle = M\zeta k_B T \delta(t-t'), \] (2)

So that the noise is uncorrelated and sets the temperature \( T \). The Langevin equation in combination with equation 2 can be used to derive an equation for the mean square displacement:
\[ \langle \Delta X^2 \rangle = \frac{6k_B T}{M\zeta} (|t-t'| + \zeta^{-1} (\exp(-\zeta |t-t'|) - 1)). \] (3)

The first term in this equation describes linear increase of the mean square displacement due to diffusion. More information about this is given in the next section. The second term does not increase linearly. This term can be neglected, except for the case where the time scale is small compared to \( \frac{1}{\zeta} \). This is called the ballistic regime. So a requirement for the use of Langevin dynamics to determine the diffusion is that the time scale between collisions should be small compared to the time scale used in simulations. Only than the movement of the particles is described by diffusion [4].

2.2 Diffusion

For timescales larger than \( 1/\zeta \) and no physical constrains, the movement of particles suspended in a fluid due to their interaction can be described by Brownian motion. Particles move through the fluid and change direction due to collisions with other particles and the solvent molecules. Then the path of the particles is changed direction. For Euclidean space, Einstein described this diffusion with the formula \( \langle \Delta X^2 \rangle = 2dD\Delta t \) [5]. In this formula, \( \langle \Delta X^2 \rangle \) is the mean square
displacement, $d$ is the number of dimensions in which the particles can move, $D$ is the diffusion constant and $t$ is the time.

So for two dimensional space the mean square displacement is given by $\langle \Delta X^2 \rangle = 4D\Delta t$. This is the diffusion in both directions. For a cylinder, these directions are given by the longitudinal direction ($\hat{h}$) and the circumferential direction ($\hat{\Theta}$). In this project the diffusion in each of these directions is determined separately. The summation over these directions gives the total mean square displacement, $\langle \Delta X^2 \rangle = \sum_i \langle \Delta X_i^2 \rangle$, where $\langle \Delta X_i^2 \rangle$ is the mean square displacement in one direction. So for the current situation the mean square displacement in both directions is given by:

$$\langle \Delta X_h^2 \rangle = 2D_h \Delta t;$$
$$\langle \Delta X_\Theta^2 \rangle = 2D_\Theta \Delta t.$$ (4)

For planar diffusion the two diffusion constants in this formula are equal. On curved surfaces this is not necessarily true, because crowding effects depend on curvature.

Combining the information about Langevin dynamics with this information about the diffusion constant, a new formula for the diffusion constant can be derived. This formula is applicable for the case of one particle that interacts only with the fluid. Comparing equation 4 and equation 3 gives:

$$D = \frac{k_B T}{M\zeta}.$$ (5)

Einstein derived the same formula for the diffusion constant in a different way [5]. $M\zeta$ is here the coefficient of friction, described by $M\zeta = 6\pi\eta R$. In this formula $\eta$ is the viscosity, and $R$ the radius of the diffusing particles. In combination with equation 4 the diffusion can be described by:

$$\langle \Delta X_h^2 \rangle = \langle \Delta X_\Theta^2 \rangle = \frac{2k_B T}{M\zeta} \Delta t.$$ (6)

So in the limit of very low densities, the diffusion should be described by above formula. Another interesting limit is the limit of the radius to infinity. In this case the surface is approximately flat, so due to symmetry the diffusion constant of both directions should be equal.

### 2.3 Surface density

On a two dimensional infinite surface, a hexagonal lattice gives the maximum coverage of a surface by spheres. The maximum surface density is in this case $\eta_{max} = 0.907$ [6]. Due to boundary conditions the maximum can be reduced. The maximum value of the surface density on a flat surface can, due to this effect, vary between $\eta_{max} = 0.54$ and $\eta_{max} = 0.907$ [7]. This is also the case for the particles on a cylinder. In that case the width of the sample can be compared to the circumference of the cylinder. So the surface density does in this case not represent the number of particles divided by the number of particles that fit on the cylinder.

In the case of a three dimensional simulation of spherical particles on a cylinder, the packing density is not exactly given by the surface of circles divided by the surface of the cylinder. The surface of spheres on the surface of the cylinder is the surface represented by the overlap in the surface of the cylinder and the volume of the sphere. So the radius of the particles on the cylinder is not constant. In this project, this effect is taken into account when calculating the surface density.
To determine the surface density, first the line of overlap of one particle and the cylinder is determined. By assuming the cylinder is oriented along the z-axis, the equation for the cylinder is given by $x^2 + y^2 = R^2$, in which $x$, $y$ and $z$ are Cartesian coordinates and $R$ is the radius of the cylinder. As described, the middle points of the particles overlaps with the circumference of the cylinder. For a particle with its middle point at $(R, 0, 0)$, the surface is given by $(x - R)^2 + y^2 + z^2 = r^2$. $r$ represents the radius of the particle. Due to the symmetry, the surface of this particle on the cylinder is identical to the surface of other particles at any other place on the cylinder.

The line of intersection of the particle and the cylinder must satisfy both equations. So by inserting one equation in the other, we find

$$z^2 = r^2 + 2R(x - R)$$

or in cylindrical coordinates

$$z^2 = r^2 + 2R^2(\cos(\theta) - 1).$$

The width of the particle on the surface of the cylinder is given by $b = R\theta$, so the circumference of the surface of a particle on the cylinder is given by:

$$z^2 = r^2 + 2R^2 \left( \cos \left( \frac{b}{R} \right) - 1 \right). \quad (7)$$

Figure 1: Surface of spherical particles on a cylinder for varying values of $\frac{R}{r}$. For small values of this ratio, the surface has a higher width than height. For big values, the surface is almost circular.
Some examples of the shapes of spherical particles on a cylinder are given in figure 1. When the limit to infinity of the ratio of $R$ and $r$ is taken, the surface should be a circle. In this case, a Taylor expansion gives $\cos \left( \frac{b}{R} \right) = 1 - \frac{b^2}{2R^2}$ (because $b \approx r$). Using this in equation 7 gives $z^2 + b^2 = r^2$, which is the equation of a circle, as it should be.

Now the surface of one particle can be calculated by integrating equation 7. This multiplied by the number of particles ($n$) and divided by the surface of the cylinder (with height $h$) gives the surface density. So:

$$\eta = \frac{n \int_{b_{\min}}^{b_{\max}} \sqrt{r^2 + 2R^2 \cos \left( \frac{b}{R} \right) - 1} \, db}{2\pi Rh}. \tag{8}$$

Relative differences between the surfaces used in comparison with circles for some values of $\frac{R}{r}$ are shown below. From this it becomes clear that the differences are very small.

$$\frac{\Delta \eta}{\eta} \left( \frac{R}{r} \rightarrow 5 \right) = 0.00031;$$
$$\frac{\Delta \eta}{\eta} \left( \frac{R}{r} \rightarrow 2 \right) = 0.0079;$$
$$\frac{\Delta \eta}{\eta} \left( \frac{R}{r} \rightarrow 1 \right) = 0.033. \tag{9}$$

In the case of a three dimensional simulation of particles on a cylinder, there is an additional effect that affects the stacking of particles. As described, the radius of the cylinder is defined as the distance from the centre of the cylinder to the middle points of the particles. In the circumferential direction, two particles already touch each other before they touch on the surface of the cylinder. To illustrate this, figure 2 shows four and five particles with their middle point on a cylinder. The particles in these examples hit each other in the circumferential direction. The outermost dotted circle represents the cylinder and the dotted inner circle the cylinder where particles hit each other. It is clearly visible there is a difference between these two cylinders. From this picture it also becomes clear that fewer spheres fit on a cylinder than circles fit on an unfolded cylinder. This is due the steric constraint, that in the case of spheres, the area between the surfaces cannot be fully covered. In the limit where the radius of the cylinder is infinity times bigger than the radius of the spheres, this difference disappears.

In the longitudinal (flat) direction, there is no such effect. Therefore the angle of impact of two particles influences the distance between the particles, at the moment of a collision. For example, the distance between the particles when they reach each other in the longitudinal direction is not changed, in the circumferential direction the distance is changed most and at every angle between these two extremes the distance is altered partly. In this project, this effect is not taken into account when determining the surface density.
Figure 2: Simplified representation of most dense packing of spherical particles on a cylinder in the case of exactly four (a) or five (b) fitting particles in the circumferential direction, shown in the longitudinal direction. The black lines in this picture represent the surface of the particles. The outer dotted line represents the surface of the cylinder. The inner dotted circle represents the cylinder at which these particles hit each other when they hit in exactly the circumferential direction.

2.4 Number of fitting particles

Figure 2 can also be used to determine the number of particles that fit in the circumferential direction. For this, the angle the particles cover of the cylinder is determined. For this, we first determined the angle on the surface of the particles covered by the inner cylinder in figure 2. This angle depends on the radius of the cylinder and so on the number of particles fitting on one circumference. Adding the angles of all particles with each other gives a total angle of $2\pi$, to make sure a circle is formed. So half the angle on the surface of the particles is given by:

$$\theta = \frac{1}{2} \left( \pi - \frac{2\pi}{n_f} \right). \quad (10)$$

In this formula, $n_f$ is the number of particles that fit next to each other on one circumference of the cylinder. Figure 3 and 4 make the used calculation more clear.

With this information, the length on one side of a regular polygon with $n$ corners can be calculated. The expression for this is given by:

$$l = 2r \sin (\theta) = 2r \cos \left( \frac{\pi}{n_f} \right). \quad (11)$$

From the geometry of figure 3 and 4 it becomes clear that the radius of the cylinder at which the particles hit each other when they are exactly next to each other, is given by $\Lambda = R \cos \left( \frac{\pi}{n_f} \right)$. The length form equation 11 can be used to determine half the corner that particles use on a cylinder. This is equal to $\Theta = \arcsin \left( \frac{l}{2r} \right) = \arcsin \left( \frac{1}{\Lambda} \right)$. 

6
Figure 3: Simplified representation of most dense packing of spherical particles on a cylinder in the case of exactly four (a) or five (b) fitting particles in the circumferential direction, shown in the longitudinal direction. The black lines in this picture represent the surface of the particles. The outer dotted line exactly surrounds the cylinder, while the inner dotted line exactly surrounds the cylinder at which these particles hit each other when they hit in exactly the circumferential direction.

Now all the information needed to determine the number of particles that fit on the circumference of the cylinder is found. This is given by the total angle of the cylinder divided by the angle of one particle:

\[ n_f = \frac{2\pi}{2\Theta} = \frac{\pi}{\arcsin \left( \frac{r}{R} \right)} \]  

(12)

In the limit of \( R \) to infinity the number of fitting particles also goes to infinity, as it should. The number of fitting particles can be used to give more inside in what a certain ratio between the the radius of the cylinder and the radius of the particles means.
Figure 4: Simplified representation of one spherical particle on a cylinder in the case of exactly four (a) or five (b) fitting particles in the circumferential direction, shown in the longitudinal direction. The circular black line in this picture represent the surface of the particle. The circular dotted line represents the cylinder where the particles hit each other. In this figure, $r$ and $\Lambda$ are respectively the radius of the particle and the cylinder. $\theta$ is half the angle covered on a particle and $\Theta$ is half the angle covered on the cylinder. $l$ is the length of one side of a regular polygon with $n$ corners inside the cylinder.

### 2.5 Lennard-Jones potential

The Lennard-Jones potential is a mathematical model that approximates the interaction between two particles. The potential consist of a repulsive term and a attractive term. Particles that are close to each other repel each other due to Pauli repulsion. Particles at larger distances attract each other due to the Van der Waals force. The expression of the Lennard-Jones potential is given by: [8]

$$V_{LJ} = 4\epsilon \left( \left( \frac{\sigma}{d} \right)^{12} - \left( \frac{\sigma}{d} \right)^{6} \right). \tag{13}$$

In this formula, $\epsilon$ is the depth of the potential well, $\sigma$ is the distance from the centre of a particle where the potential is zero and $d$ is the distance between the particles.

To simplify the model, in this project only the repulsive part of the potential is used. For this, the potential is first increased with $\epsilon$, so the lowest point of the potential is at $V_{LJ} = 0$. Then the part right of $\sigma$ is deleted. In figure 5, the process of changing the potential is shown.
Figure 5: From left to right the process of changing the Lennard-Jones potential, so only the repulsive part is left. In graph a, the normal Lennard-Jones potential is shown. In graph 2, the potential is increased with $\epsilon$ and in graph c the attractive part of the Lennard-Jones potential is removed.

After this modification, the equation for the potential is given by:

$$V_{LJ} = \begin{cases} 
4\epsilon \left( \left( \frac{d}{\sigma} \right)^{12} - \left( \frac{d}{\sigma} \right)^{6} \right) + \epsilon & \text{if } \frac{d}{\sigma} < \frac{\sigma}{2}; \\
0 & \text{if } \frac{d}{\sigma} \geq \frac{\sigma}{2}.
\end{cases} \quad (14)$$

When two particles get close to each other, they change direction due to the potential. When all kinetic energy of the particles is transferred to potential energy due to the potential, the smallest distance between two middle points of particles possible is reached. Form a mechanical point of view, the closest distance two particles can get to each other is when their surfaces touch. Because in this project, the radius of all particles are equal, this distance is $2r$. So two times the radius of a particle is equal to the distance where the kinetic energy is fully converted to potential energy. Equation 11 can be used to determine this distance.
3 Simulation method

In the first part of this chapter, the concept and assumptions of this project are described. Next we describe the simulation method. To increase the accuracy of the determination of the diffusion coefficient, we invoke an averaging method which we describe in the last section of this chapter.

3.1 Concept and assumptions

In this project, the directionality of diffusion of particles on curved surfaces is researched. For this, a cylindrical surface is chosen. This is a good first choice for the surface, because it is curved in one direction and flat in the other direction. So a comparison between the diffusion in a curved direction and a flat direction can be made. Another advantage is that the curvature of the cylinder is constant in the circumferential direction. A simplified representation of the situation is shown in figure 6. The particles in this representation are defined by the repulsive part of the Lannard-Jones potential. Only the repulsive part of this potential is used, to simplify the model.

Figure 6: Simplified representation of particles distributed over the surface of a cylinder in three dimensions.
As earlier described, the radius of a cylinder can be determined by putting the potential energy equal to the kinetic energy of a particle. In this project, $V_{LJ} = k_B T$, $\epsilon$ and $\sigma$ are chosen to be one Lennard-Jones unit, in all simulations. With formula 14, it can be determined that the radius of the particles in this case is one Lennard-Jones length unit.

3.2 Simulation

To simulate the diffusion using Langevin dynamics, the molecular dynamics package in LAMMPS is used [9]. This is a molecular dynamics program from Sandia National laboratories. The program uses neighbour lists to keep track of nearby particles. Particles are defined by their potentials in this program. In the simulations in this project, the repulsive part of a Lennard-Jones potential is used, as explained in the chapter "Theory". LAMMPS partitions the simulated domain into small sub-domains. To determine the position and velocity of the particles, the crossings of particles over the boundaries of such subdomains is registered.

An example of a script used in this program is shown in appendix A. In this script, first the region where particles can start is defined. We used a cylindrical shell for this. Then the particles are placed randomly inside this shell. In the first few time steps, a potential is used that pushes these particles to the outside of this region, till all middle points of particles are on the surface of the cylinder.

Boundaries could influence the movement of the particles. This changes the results of the simulations. So to give a good comparison between the longitudinal diffusion and the circumferential diffusion, there should be no boundaries for the particles (except that they should stay on the cylinder). That is why the top and bottom of the cylinder are rendered periodic. This means that when a particle leaves the simulation at the bottom of the cylinder, it will come back at the top. In this way an infinitely long cylinder without boundaries is created.

After the random positioning of the particles on the cylinder, the actual simulation can start. The repulsive part of the Lennard-Jones potential is turned on and the particles start to move according to Langevin dynamics. Every few time steps, the position of the particles in Cartesian coordinates, the temperature, potential energy, kinetic energy and total energy of the system are exported.

During the simulations, some of the variables in this script are varied. To change the surface density, we vary the length of the cylinder. Normally, one thousand particles are used in each simulation. This amount of particles gives enough statistics to accurately determine the diffusion. For very low densities, the number of particles is decreased to one hundred. This is done because with one thousand particles, the cylinder is much longer, so there are more sub-domains (called atom sorting bins). For very low densities there are more atom sorting bins than can be used with the used script. To do a simulation at a surface density of zero, the interaction between particles is turned off.

Another variable in our simulations is the ratio of the radius of the cylinder in comparison to the radius of the particles. This is varied by varying the radius of the cylinder. A third variable that is varied is the duration of the time steps between data exportations. To make the Ballistic regime visible, this time is reduced to 1/100 and 1/20 of a Lennard-Jones time unit. In the simulations used to determine the diffusivity, data is exported every Lennard-Jones time unit.
3.3 Transformation of data

The result of the simulations described above is a collection of datasets with the positions of particles over time in Cartesian coordinates. The datasets vary in surface density of particles on the cylinder, the radius of the cylinder compared to the radius of the particles and the duration of the time steps.

To analyse these datasets, Wolfram Mathematica [10] is used. First the coordinates are transformed to cylinder coordinates. Then the Θ-coordinate is multiplied by the radius, so the two coordinates left are the position in the longitudinal direction on the cylinder (z) and the position in the circumferential direction on the cylinder (d = ΘR). In this way it becomes easier to determine the circumferential displacements and the position of the particles can be shown in a two dimensional graph. The change in representation is shown in figure 7.

To determine the displacement of the particles, the position of the particles at time t + 1 is subtracted from the position at time t. After the configuration, the systematic contribution to the energy, as described in the part about Langevin dynamics in the chapter "Theory", keeps the energy of the system constant. So the system is balanced and the displacement is independent of the time. So the displacement can also be averaged over time to give a more accurate result. This information is used to determine the distribution of displacements.

As described earlier, in the analysis, the position of the particles is determined by their position on the cylinder in the coordinates z and b = ΘR. This means that two particles next to each other can be registered at a distance 2b from each other round Θ = π. Also when a particle moves over this determined "boundary" at Θ = π, the displacement of the particle will be registered as a displacement of 2πR.

Figure 7: Graph a shows the position of the particles in three dimensional Cartesian coordinates. After the data transformation, the data can be viewed as shown in graph b. This figure gives the positions of particles in two dimensions over the surface of the cylinders.
To solve this problem, the time steps in the simulations are chosen small enough, so it is not possible for the particles to move more in one time step than half the circumference of a cylinder. In this way, all the displacements bigger than half the circumference of the cylinder, can be corrected by taking the modulus of all values between $-\pi R$ and $\pi R$. A problem with this method, is that it is not possible to add the displacements to get the displacements at time steps with a longer duration. This can be solved by first taking the modulus of every smallest time step and then creating the larger time steps by adding these values.

In the longitudinal direction, it is also possible that particles cross the boundary. In this case, they move from the top of the cylinder to the bottom in one time step, or vice versa. Again, by using the modulus (this time from $-\frac{L}{2}$ to $\frac{L}{2}$), the correct value for one time step can be determined. By adding the correct values for one time step, the correct value for larger time steps can be determined. Four of the used Mathematica scripts to transform the data are shown in appendix B.

### 3.4 Calculation diffusion

To obtain the diffusion coefficient, the displacements are determined for multiple time steps $(X(t_0 + 1) - X(t_0), X(t_0 + 2) - X(t_0), X(t_0 + 3) - X(t_0), \text{enz})$. Then for all particles this value is squared and averaged. A linear fit trough the mean square displacement for varying duration of time steps gives $2D$.

The displacement measured from one start-time is equal to the displacement measured starting at another time. So to get a more accurate result, the displacements of particles starting at all time steps can also be averaged. Figure 8 explains this method. The Mathematica script used for this is the "Accurate diffusion determination"-script in Appendix B.

![](image.png)

**Figure 8:** Visual representation of the averaging of displacements over time for $\Delta X_2$. First the displacements at individual time steps are calculated by determining the change in position over one time step and adding the squares of these values. Then the time average of these squares is taken.
To make the results in the cases where hundred particles are used as accurate as the simulations where a thousand particles are used, the simulation time should be longer. The time needed for simulations increases non-linear with the simulated time. This is the reason why for the simulations with hundred particles, the simulation method with time averaging is used. In this way the simulation time can be reduced. The errors indicated for the data are the errors in the fit through the average mean square displacements.

In our case, thousand particles are used in most simulations. In this cases the results from this method and the method without averaging over the time steps are both accurate enough. For this simulations the number of time steps and particles is big enough to get an very accurate result. Because the averaging over starting times is time consuming, for this simulations the method without time averaging is used.
4 Results and discussion

4.1 Distribution of displacements

The first result in this project is the distribution of displacements. Figure 9 shows the distribution of displacements in the circumferential direction for a cylinder with a length of two hundred Lennard-Jones units and a radius of one Lennard-Jones unit. The surface density in this case is equal 0.63 and the number of particles that fits on the cylinder in the circumferential direction is 6. This can be computed with formula 8 and 12. From now on a red colour will be used for graphs representing the circumferential direction and a blue colour for the longitudinal direction.

Graph 9a shows the distribution when no correction is done for the passing of the "boundaries". It shows an expected distribution round $\Delta h = 0$, but also has some values round $\Delta h = 2\pi$. After the correction for these translations, the distribution is as expected, as shown in graph 9b. Same results are obtained in the longitudinal direction.

Now a comparison can be made between the distribution of displacements in the longitudinal direction and the circumferential direction. Both distributions are shown in one graph in figure 10. Also the movement of individual atoms is shown in the right picture. In this picture the dots represent the displacement compared to the previous time step in the shown direction. Clearly the distribution is not equal in both directions. In the shown case, the displacement in the circumferential direction has a broader distribution than the displacement in the longitudinal direction.

For all other datasets comparable graphs can be made. This gives comparable results. As expected, the distribution becomes more broad when lower densities are used. A comparison in the difference between longitudinal and circumferential displacement must be made to get a clearer view of this difference. For this, the diffusion will be determined in the next view sections.

![Figure 9: Distribution of displacements in the circumferential direction, for a cylinder with a length of two hundred Lennard-Jones units and a radius of one Lennard-Jones unit ($\eta = 0.63$ and $n_f = 6$). In graph a the distribution without a correction for boundary crossing is shown. In graph b this correction is made.](image)
4.2 Ballistic regime

Before the diffusion can be determined, it is important to determine when the diffusive regime starts. For this, the mean square displacement is plotted for small time steps in figure 11. In this figure, it is clearly visible that the Ballistic regime ends around one Lennard-Jones time step. As described in the chapter "Theory", the end of the Ballistic regime should be around $1/\zeta$. In the simulations, $\zeta$ is chosen to be one Lennard-Jones unit, so this corresponds to theory. Also there is no difference between the time of transition between flat surfaces and curved surfaces.

Notable is that even in the ballistic regime, there is a difference between the longitudinal displacement and the circumferential displacement. The difference gets larger as time steps get larger. The reason for this is that even in the ballistic regime, where the time steps are smaller than the average time between two collisions of a particle, some particles collide. These collisions cause the difference between the mean square displacement in the longitudinal direction and the circumferential direction. More information about the reason for this difference is given in the next sections.

Within the Ballistic regime, the longer the time steps, the higher the percentage of particles that collide with other particles, so the higher the difference between the mean square displacement in the longitudinal direction and the circumferential direction. For $\Delta t > 1$, almost all particles collided with other particles and the Ballistic regime ends.

At high densities, for longer time steps than $1/\zeta$, the displacement is still lower than in the diffusive regime. This is caused by the caging of particles. At high densities, particles are surrounded by other particles. On average it takes a number of collisions before a particle can travel past a group of particles. For time steps longer than the time needed for particles to escape from their 'Cages', the diffusive regime starts. This is the last part of the graph shown in figure 11. This is the regime where the diffusion constant can be determined.

Figure 10: Distribution of displacements for a cylinder with $\eta = 0.66$, $R = 0.64$ and $n_f = 3.5$. In graph a the distribution in the circumferential direction (red) and longitudinal direction (blue) are shown in one figure. Figure b shows the displacement compared to the starting point at (0,0).
For low surface densities, there is no caging regime, because the particle density is not high enough to surround a particle. In this case the diffusive regime starts after the Ballistic regime. At very high densities, particles stay trapped and the diffusive regime never starts. From this can be concluded that when determining the diffusion constant, only big enough time steps should be taken into account and the diffusion can not be determined at too high densities.

### 4.3 Difference in diffusion

Now the diffusion can be determined. For this, first again a graph of the mean square displacement over time is made, but this time for time steps from minimal one Lennard-Jones unit. In figure 12 four graphs of the mean square displacement over time are shown. In the next paragraphs these graphs will be disused one by one.

Graph 12a shows the average mean square displacement at a high surface density of $\eta = 0.63$ (and $R = 1$). The diffusion in the circumferential direction is in this case given by $D = 0.7532 \pm 0.0001$ and in the longitudinal direction by $0.3656 \pm 0.0003$. So in this case there is clearly a difference between both directions. In the research by Kusters et al., this difference was also indicated [3].
The earlier done research on this topic already gives a good explanation for the reason why there is more diffusion in the circumferential direction than in the longitudinal direction at high densities [3]. At high densities, the particles move only very small pieces, because the collide very often with other particles. The only possibility for big displacements is when the particles move in clusters. This means that multiple particles next to each other move all in the same direction.

For cooperative movement, there are less particles needed in the circumferential direction than in the longitudinal direction, because only a limited amount of particles fit in the circumferential direction. In the longitudinal direction the particles along the whole cylinder must move. The chance that big amounts of particles move in the same direction is smaller than small amounts, so there will be more cluster displacement in the circumferential direction. This is the reason why there is on average more displacement in the circumferential direction.

Graph 12b shows the average mean square displacement at a low density of $\eta = 0.105$ (and $R = 1$). The diffusion in the circumferential direction is in this case given by $D = (0.6084 \pm 0.0005$ and in the longitudinal direction by $0.5458 \pm 0.0003$. So still at a low density there is a difference between both directions. This time there is a difference with the measurements done in the earlier conducted two dimensional simulations.
An important question is why there can be a difference in diffusion in the three dimensional simulation, while there is no difference in the two dimensional situation. As described, in the two dimensional situation the difference between the diffusion in the longitudinal direction and the circumferential direction is caused by movement in clusters. At low densities, particles are far from each other, so this can’t be the case at low densities.

A possible explanation of this difference is the blocking of particles in the longitudinal direction by other particles. In the case of a three dimensional simulation, it can be that a particle travelling in the longitudinal direction does collide with another particle, where it in the two dimensional simulation would not collide. In figure 13 this difference is shown. This is an abstract representation of particles and circles on a cylinder, looking in the longitudinal direction of the cylinder. The particles in the three dimensional case overlap inside the cylinder, so will hit each other in the longitudinal direction. In the two dimensional case they pass each other or when they also have a circumferential velocity, they hit each other from the side.

So the particles in the three dimensional simulation have a higher chance to hit each other from the top. Due to the same reason there is a smaller chance the particles get next to each other, so the chance of particles to hit in the circumferential direction is smaller. In a not dense system, the more particles hit in a certain direction, the less they diffuse. So this could cause the difference. An additional reason is that the surface of particles are broader than they are long on a cylinder, as described in the chapter "Theory". This also increases the chance of collisions in the longitudinal direction.

Graph 12c shows the case where the density is minimal. In this case, a particle never meets another particle. To simulate this, the interaction between particles is turned off. The diffusion constant is in this case given by 0.9777 ± 0.0005 in the longitudinal direction and 0.9786 ± 0.0005. So in this case the diffusion in both directions is equal, as expected. In theory, the diffusion constant should be equal to $D = \frac{k_B T}{M \zeta}$, which is with the used parameters equal to 1. So the simulations show a diffusion constant very close to the theoretical diffusion constant.
Graph 12d gives a situation where the radius of the cylinder is ten times as big as the radius of a particle. In this case, there are 31.4 particles that fit round the cylinder. The diffusion constant in this case is given by $0.2016 \pm 0.0001$ in the longitudinal direction and by $0.2091 \pm 0.0003$ in the circumferential direction. So the diffusion in the circumferential direction is a little bit higher.

In the limit $\frac{R}{r} \rightarrow \infty$, the difference between the longitudinal direction and circumferential direction should disappear, because then the surface becomes a flat surface. The diffusion constants are not completely equal, but are almost equal. This is as expected, because the effect of the curvature is minimized, but not completely gone in this case.

4.4 Variation of density

To get a better view of the relation between the surface density and the difference in diffusion, measurements are done for varying surface densities. The results of these measurements for the cylinder with radius $R = 1$ are shown in figure 14a. Six particles fit in the circumferential direction on this cylinder. Graph 14b shows the ratio of the diffusion constant in the circumferential direction and the longitudinal direction.

From graph 14a it is clear that the diffusion increases for lower surface densities, as expected. The highest density with moving particles is around $\eta = 0.7$. Between the lowest possible density and the highest possible density, there is everywhere a difference between the diffusion in the longitudinal direction and the circumferential direction.

From graph 14b it becomes clear that the relative difference between the diffusion in the longitudinal direction and the circumferential direction decreases with decreasing surface density. So apparently the effect of the cooperative movement of particles is bigger than the effect of the blocking of particles in the longitudinal direction. Both effects get smaller when surface density decreases.

![Figure 14 a and b](image-url)
That both effects decrease when the surface density decreases is expected. Clustered movement becomes less important at lower densities because the lower the density, the easier the particles can pass each other without moving in clusters. For the blocking of particles, at lower density there are less collisions between particles, so that effect also gets smaller.

In the graph of the ratio of circumferential and longitudinal diffusion a pattern is visible. In general the ratio decreases with decreasing surface density, but the data also shows a non-monotonic dependence. The higher the surface density, the narrower and bigger the oscillations differences. Graph 14a even shows that it is possible that the diffusion decreases, when the surface density decreases.

A possible explanation for this non-monotonic behaviour is the ordering of the particles. More information about this is given in the the section "Ordering of particles". A qualitative analysis of the pattern requires more data. This could possibly be obtained in a future research. Other graphs give comparable results to the result shown in figure 14. These graphs can be found in appendix C.

4.5 Variation of radius

Something else that can be varied is the ratio of the radius of the cylinder and the radius of the particles. Figure 15 shows dependency of the diffusion on the surface density for the cylinders with $\frac{R}{r} = 1$, $\frac{R}{r} = 1.6$, $\frac{R}{r} = 2$, and $\frac{R}{r} = 10$. As expected, the difference in diffusion becomes smaller when a smaller radius is used. In the case of $\frac{R}{r} = 10$, there is even nearly no difference visible anymore, as expected.

So the smaller the radius of the cylinder, the bigger the relative difference between the circumferential direction and the longitudinal direction. But this is not the only thing notable. Not only the circumferential diffusion is higher in the case of a small cylinder, also the diffusion in the longitudinal direction is lower.

A possible explanation for the higher diffusion in the circumferential direction, is the cooperative movement. At very low densities this effect is negligible. This agrees with the data, because at low densities the increased circumferential diffusion disappears. In the extreme case of an equal radius of the cylinder and the particles, the diffusion even decreases. A possible explanation for the lower diffusion in the longitudinal direction, is the blocking of particles, as described in the section "Difference in diffusion". In the extreme case of an equal radius of the cylinder and the particles, the longitudinal diffusion stays for a wide range of surface densities very small in comparison to a flat surface.

It is also possible to create a graph where the diffusion is shown for varying radius of a cylinder at constant surface density. This is not done in this project, because the surface density is not completely well defined, as described in the section "Surface density". There are already two dimensional simulations done for this case [3]. In future research this may be done in three dimensional simulations.
4.6 Ordering of particles

As described earlier, a possible explanation of the non-monotonic behaviour in the ratio of the diffusion in the circumferential direction and the longitudinal direction is the ordering of the particles. If the particles are ordered rectangular, the circular movement is easier because the first particle is also the last particle in a cluster movement (and so on).

To analyse this, the structure at a high and low ratio compared to close surface densities in figure 14 is shown in figure 16. For this, again the structure is plotted with coordinates $b$ and $z$. The top figure shows the structure for a high ratio and the bottom picture for a low ratio.

Both surface densities contain parts where an exactly circumferential cooperative motion is possible and parts where this is not possible. The difference is the ratio of occurrence of these areas. For the relatively low ratio, in most places the ordering doesn’t make it possible to move exactly circumferential. For the relatively high ratio, this is possible in most places. As described, for low densities the oscillations are less evident. A possible reason for this is that the ordering of the particles also becomes less clear at lower surface densities.

Figure 15: The diffusion in the longitudinal (blue) en circumferential (red) direction for varying surface density.
In the earlier conducted two dimensional simulations, the dependency of the ratio of the diffusion in the circumferential direction and the longitudinal direction was indicated as a cause for the non-monotonic behaviour of the diffusion when the radius of the cylinder is varied [3]. The dependency when the surface density is varied is an extra effect shown in this research. Yet it is possible that the structure indicated in the two dimensional simulations is different from the three dimensional simulations, due to the effects described in the sections "Surface density" and "Number of fitting particles".
5 Conclusion and future research

5.1 Conclusion

In this project, the effect of curvature on the directionality of diffusion is researched. For this, the diffusion of particles in the circumferential en longitudinal direction on a cylinder are compared. As an improvement to earlier research with two dimensional simulations, three dimensional simulations are done. The first result in this project is that, similar to what was found for two dimensional simulations, for small radius of the cylinder in comparison to the radius of the particles, the circumferential component of the diffusion coefficient is larger than the longitudinal component.

Moreover, in the Ballistic regime we did not observe difference between the time at which the the system becomes diffusive for flat surfaces and curved surfaces. The difference in diffusion in the circumferential direction and the longitudinal direction turned out to be highest for small cylinders in comparison to the radius of the particles and high surface densities. Even at low densities there are still differences between the diffusion in the circumferential direction and the longitudinal direction.

An explanation for the difference at high densities is that the particles move in clusters. Due to the small amount of particles in the circumferential direction, there is a bigger chance on cooperative movement in this direction. An explanation for low densities is that the particles are blocked by other particles in the longitudinal direction. They hit each other due to the curvature of the cylinder.

As expected, the diffusion coefficient is higher at low densities than at high densities. The higher the density, the higher the relative difference between the diffusion in the circumferential direction and the longitudinal direction. The anisotropy decreases at lower surface densities. Our data suggests that the relative difference between the diffusion in the circumferential direction and the longitudinal direction varies non-monotonic with the surface density. This could be caused by the ordering of the particles on the cylinder. When the ordering allows exactly circumferential cooperative movement at many places, the diffusion is relatively high.

To conclude, the three dimensional simulations agree with the two dimensional simulations since there is a difference between the diffusion in the circumferential direction of a cylinder and the longitudinal direction of the cylinder. In both cases the difference is higher at higher densities and at a smaller ratio of the radius of the cylinder and the particles. New insights due to the three dimensional simulations are that there is still a difference in the diffusion at low densities and that our data suggests that the diffusion depends non-monotonic on the surface density.

5.2 Future research

In this project the diffusion of particles on a cylinder is researched in three dimensional simulations. This is a first step to the description of diffusion over curved surfaces. There are many ways in which this research can be continued to improve the knowledge about the diffusion of particles over curved surfaces.

First of all, there are still some questions unanswered about the diffusion of particles on cylinders. The non-monotonic dependency of the diffusion on the surface density can be made more quantitative by doing more measurements. Also the dependency on the radius of cylinders can be made more quantitatively. For this an accurate formulation of the surface density is needed.
Another way in which this research can be continued, is by doing research with different shapes of surfaces. An example of next shapes that could be researched, are cylinders that have a longitudinally dependent radius, curved cylinders or a cylinder with a boundary at one of its ends. In this way other effects can be taken into account.

A last way in which this research can be improved is by doing more realistic simulations by including other effects or by doing experimental measurements to the diffusion of particles on curved surfaces. When experimental measurements agree with the simulations, this gives evidence that the used model is correct.
6 Sources


A  Appendix

A.1  LAMMPS script

```plaintext
# Variables:
variable radius equal 1.0
variable box_size equal "100 * v_radius"
region total block -{box_size} {box_size} & -{box_size} {box_size} & -{box_size} {box_size}

atom_style atomic
create_box 1 total

# Create sphere as region:
variable inner_r equal "0.85 * v_radius"
variable outer_r equal "1.0 * v_radius"

region cylinder_inner cylinder z 0 0 {inner_r} -{box_size} {box_size} side out
region cylinder_outer cylinder z 0 0 {outer_r} -{box_size} {box_size} side in
region cylinder_shell intersect 2 cylinder_inner cylinder_outer

# Create atoms:
create_atoms 1 random 1000 1 cylinder_shell
mass 1 1.0

# Fixes:
fix temp_0 all langevin 1.0 1.0 1.0 1
fix cylinder all nve/manifold/rattle 1.0e-4 4 cylinder {radius}

# Pair style
pair_style soft 2.1225
pair_coeff * * 1.0 1.1225
variable prefactor equal ramp(0,3000)
fix 1 all adapt 1 pair soft a * * v_prefactor

thermo 100000
thermo_style custom step temp pe ke etotal
dump trajectories_lj all xyz 10000 trajectories_lj.xyz

run 1000000

unfix 1
pair_style lj/cut 1.1225
pair_coeff * * 1.0 1.0
pair_modify shift yes

run 7000000
```
A.2 Mathematica scripts

A.2.1 Basic plot

Clear["Global`*""]

n = 1000;
x = 50;

SetDirectory["C:\Users\s121438\Desktop\BEP\Simulaties\R1\R1L180"];

Data = Import["trajectories_lj.xyz", "table"];
Needs["VectorAnalysis""]

PartData = Partition[Data, n + 2];

TransData = Transpose[PartData[[x]][[3 ;; n + 2]]];
TransDataS = Transpose[PartData[[x + 1]][[3 ;; n + 2]]];

DataSet = Transpose[TransData[[2 ;; 4]]];

ListPointPlot3D[DataSet, PlotStyle -> {PointSize[0.025], Black, 20},
AspectRatio -> 1, AxesLabel -> {"x", "y", "z"}]

r\[Theta]h = CoordinatesFromCartesian[#1, Cylindrical] & ;
FormData = Partition[DataSet, 1];
DataCyl = Apply[r\[Theta]h, FormData, {1}];
DataCyl2 = DataCyl[[All, 2 ;; 3]];
DataCyl3 = DataCyl2;
R = 1/n Total[DataCyl[[All, 1]]]
DataCyl3[[All, 1]] = DataCyl2[[All, 1]] R;

ListPlot[DataCyl3, PlotStyle -> {PointSize[0.035], Black},
AspectRatio -> Automatic, PlotRange -> All, Frame -> True,
FrameLabel -> {"b", "z"}, FrameStyle -> 20,
FrameTicks -> {{{-25, -20, -15, -10, -5, 0, 5, 10, 15, 20, 25},
None}, {{-5 \[Pi], 0, 5 \[Pi]}, None}}]

A.2.2 Displacement diagram

Clear["Global`*""]

n = 1000;
T = 650;
H = 200;
dT = 100;
\[Tau] = 50;

SetDirectory["C:\Users\s121438\Desktop\BEP\Simulaties\R1\R1L180"];

Data = Import["trajectories_lj.xyz", "table"];
Needs["VectorAnalysis""]

DataSel = Data[[1 ;; T (n + 2)]]; PartData1 = Take[DataSel, {3, -2}];
PartData2 = Partition[PartData1, n, n + 2];
PartData3 = Partition[Flatten[PartData2], 4];
TransData = Transpose[PartData3]; TransData2 = Transpose[TransData[[2 ;; 4]]];

r[\[Theta]h] = CoordinatesFromCartesian[#, Cylindrical] &;
DataSet = Partition[TransData2, 1];
DataCyl = Apply[r[\[Theta]h], DataSet, {1}];
DataCyl2 = DataCyl[[All, 2 ;; 3]]; DataCyl3 = DataCyl2;
RData = Partition[DataCyl1, n];
R = 1/(n (T - dT)) Total[Flatten[RData[[dT ;; T - 1, All, 1]]]]
DataCyl13[[All, 1]] = DataCyl12[[All, 1]] R;
DataCyl14 = Partition[DataCyl13, n];

DDataC1 = DataCyl14[[2]][[All, 1]] - DataCyl14[[1]][[All, 1]]; Do[DDataC1 = Join[DDataC1, DataCyl4[[n]][[All, 1]] - DataCyl4[[n - 1]][[All, 1]]], {n, 3, Length[DataCyl4]}]
DDataL2 = Partition[Flatten[DDataC1], n];

DDataC1 = DataCyl14[[2]][[All, 2]] - DataCyl14[[1]][[All, 2]]; Do[DDataL1 = Join[DDataL1, DataCyl4[[n]][[All, 2]] - DataCyl4[[n - 1]][[All, 2]]], {n, 3, Length[DataCyl4]}]
DDataL2 = Partition[Flatten[DDataL1], n];

MDataL = Mod[DDataL2 + 1/2 H, H] - 1/2 H;
MData = Partition[Partition[Riffle[Flatten[MDataC], Flatten[MDataL]], 2], n];

NDataC = Sum[MDataC, {i, dT + 1, dT + \[Tau]}]; Do[MDataC1 = Join[MDataC, SumDataC, {i, t + 1, t + \[Tau]}]], {t, dT + 1, Length[MDataC] - \[Tau]}]
NDataL = Sum[MDataL, {i, dT + 1, dT + \[Tau]}]; Do[MDataC1 = Join[MDataL, SumDataL, {i, t + 1, t + \[Tau]}]], {t, dT + 1, Length[MDataL] - \[Tau]}]

NData = Partition[Riffle[Flatten[NDataC], Flatten[NDataL]], 2];

Histogram[DDataC2[[dT ;; T - 2]], {0.1}, "Probability", Frame -> True, FrameLabel -> {"\[CapitalDelta]\[Theta]h", "!\!\\(\*SubscriptBox\\(\(n\), \(i\)\)\\)\\/!\\(\*SubscriptBox\\(\(n\), \(tot\)\\)\\)"}, ChartStyle -> Red, FrameStyle -> 22]
Histogram[DDataL2[[dT ;; T - 2]], {5}, "Probability", Frame -> True, FrameLabel -> {"\[CapitalDelta]\[Theta]z", "!\!\\(\*SubscriptBox\\(\(n\), \(i\)\\)\\)\\/!\\(\*SubscriptBox\\(\(n\), \(tot\)\\)\\)"}, ChartStyle -> Blue, FrameStyle -> 22]
Histogram[{Flatten[MDataC[[dT ;; T - 2]]], Flatten[MDataL[[dT ;; T - 2]]]}, {-1.5, 1.5, 0.1}, "Probability", Frame -> True, FrameLabel -> {"\[CapitalDelta]\[Theta]z", "!\!\\(\*SubscriptBox\\(\(n\), \(i\)\\)\\)\\/!\\(\*SubscriptBox\\(\(n\), \(tot\)\\)\\)"}, ChartStyle -> {Red, Blue}, FrameStyle -> 20]
A.2.3 Accurate diffusion determination

\[f(x, y) = \frac{1}{2 \pi \sigma^2} \exp\left(-\frac{x^2 + y^2}{2\sigma^2}\right)\]

\(H = 180;\)  
\(n = 100;\)  
\(T = 650;\)  
\(dT = 100;\)  
\(nn = 100;\)  

SetDirectory["C:\Users\s121438\Desktop\BEPSimulaties\R1\R1L180"];  
Data = Import["trajectories_lj.xyz", "table"];  
Needs["VectorAnalysis"]  

DataSel = Data[1 ;; T (n + 2)];  
PartData1 = Take[DataSel, {3, -2}];  
PartData2 = Partition[PartData1, n, n + 2];  
PartData3 = Partition[Flatten[PartData2], 4];  
TransData = Transpose[PartData3]; TransData2 = Transpose[TransData[[2 ;; 4]]];  
r\(\theta\)h = CoordinatesFromCartesian[#, Cylindrical] \&;  
DataSet = Partition[TransData2, 1];  
DataCyl = Apply[r\(\theta\)h, DataSet, {1}];  
DataCyl2 = DataCyl[[All, 2 ;; 3]];  
DataCyl3 = DataCyl2;  
RData = Partition[DataCyl, n];  
R = 1/(n (T - dT)) Total[Flatten[RData[[dT ;; T - 1, All, 1]]]]  
DataCyl3[[All, 1]] = DataCyl2[[All, 1]] R;  
DataCyl4 = Partition[DataCyl3, n];  

DDataC1 = DataCyl4[[2]][[All, 1]] - DataCyl4[[1]][[All, 1]];  
Do[DDataC1 = Join[DDataC1, DataCyl4[[i]][[All, 1]] - DataCyl4[[i - 1]][[All, 1]]], {i, 3, T - 1}];  
DDataC2 = Partition[Flatten[DDataC1], n];  

DDataL1 = DataCyl4[[2]][[All, 2]] - DataCyl4[[1]][[All, 2]];  
Do[DDataL1 = Join[DDataL1, DataCyl4[[i]][[All, 2]] - DataCyl4[[i - 1]][[All, 2]]], {i, 3, T - 1}];  
DDataL2 = Partition[Flatten[DDataL1], n];  

MDataC = Mod[DDataC2 + \[Pi\] R, 2 \[Pi\] R] - \[Pi\] R;  
MDataL = Mod[DDataL2 + 1/2 H, H] - 1/2 H;  
MData = Partition[Partition[Riffle[Flatten[MDataC], Flatten[MDataL]], 2], n];  
GDataC = Transpose[MDataC];
GDataL = Transpose[MDataL];

TTDataL = Table[1/(nn (T - 2 - dT - dt)) Total[
Table[Total[GDataL[[d, t ;; t + dt]]]^2, {t, dT + 1, T - 2 - dt}],
{d, 1, nn}], {dt, 0, T - dT - 3}];

TTDataC = Table[1/(nn (T - 2 - dT - dt)) Total[
Table[Total[GDataC[[d, t ;; t + dt]]]^2, {t, dT + 1, T - 2 - dt}],
{d, 1, nn}], {dt, 0, T - dT - 3}];

pL = ListPlot[TTDataL[[1 ;; T - dT - 250]], PlotRange -> Full,
PlotStyle -> Blue];
pC = ListPlot[TTDataC[[1 ;; T - dT - 250]], PlotRange -> Full,
PlotStyle -> Red];
Show[pL, pC, Frame -> True,
FrameLabel -> {"\[CapitalDelta]t", \[CapitalDelta]X^2},
FrameStyle -> 18]

rL = NonlinearModelFit[TTDataL[[1 ;; T - dT - 250]], a \[Tau],
a, \[Tau]]; rC = NonlinearModelFit[TTDataC[[1 ;; T - dT - 250]], a \[Tau],
a, \[Tau]];
rL["ParameterTable"]
rC["ParameterTable"]

Show[Plot[rL[\[Tau]], \[Tau], 0, T - dT - 50], PlotStyle -> Blue],
Plot[rC[\[Tau]], \[Tau], 0, T - dT - 50], PlotStyle -> Red],
Frame -> True,
FrameLabel -> {\[CapitalDelta]t, \[CapitalDelta]X^2},
FrameStyle -> 18]

Show[Plot[rC[\[Tau]], \[Tau], 0, T - dT - 50], PlotStyle -> Red, pC,
Frame -> True,
FrameLabel -> {\[CapitalDelta]t, \[CapitalDelta]X^2},
FrameStyle -> 18]

Show[pL, Plot[rL[\[Tau]], \[Tau], 0, T - dT - 50],
PlotStyle -> Blue], Frame -> True,
FrameLabel -> {\[CapitalDelta]t, \[CapitalDelta]X^2},
FrameStyle -> 18]

pLLL = ListLogLogPlot[TTDataL, PlotRange -> Full, PlotStyle -> Blue];
pLLC = ListLogLogPlot[TTDataC, PlotRange -> Full, PlotStyle -> Red];
Show[pLLL, pLLC, Frame -> True,
FrameLabel -> {\[CapitalDelta]t, \[CapitalDelta]X^2},
FrameStyle -> 18]

dL = ListPlot[rL["FitResiduals"], PlotStyle -> Blue];
dC = ListPlot[rC["FitResiduals"], PlotStyle -> Red];
Show[dL, dC, Frame -> True,
FrameLabel -> {\[CapitalDelta]t, \[Delta]\[CapitalDelta]X^2},
FrameStyle -> 18]
### A.2.4 Fast diffusion determination

Clear["Global`**"]

\(H = 180;\)
\(n = 1000;\)
\(T = 650;\)
\(dT = 100;\)

SetDirectory["C:\Users\s121438\Desktop\BEP\Simulaties\R1\R5L180"];
Data = Import["trajectories_lj.xyz", "table"];
Needs["VectorAnalysis`"]

DataSel = Data[[1 ;; T (n + 2)]];  
PartData1 = Take[DataSel, {3, -2}];  
PartData2 = Partition[PartData1, n, n + 2];  
PartData3 = Partition[Flatten[PartData2], 4];

TransData = Transpose[PartData3]; TransData2 = Transpose[TransData[[2 ;; 4]]];

\(r(\theta)h = \text{CoordinatesFromCartesian}[\#, \text{Cylindrical}] \ & ;\)
DataSet = Partition[TransData2, 1];
DataCy1 = Apply[r(\theta)h, DataSet, {1}];
DataCy12 = DataCy1[[All, 2 ;; 3]];
DataCy13 = DataCy12;
RData = Partition[DataCy1, n];
R = 1/(n (T - dT)) Total[Flatten[RData[[dT ;; T - 1, All, 1]]]]
DataCy13[[All, 1]] = DataCy12[[All, 1]] R;
DataCy14 = Partition[DataCy13, n];

DDataC1 = DataCy14[[2]][[All, 1]] - DataCy14[[1]][[All, 1]];
Do[DDataC1 = Join[{DDataC1, DataCy14[[i]][[All, 1]] - DataCy14[[i - 1]][[All, 1]]}], {i, 3, T - 1}]
DDataC2 = Partition[Flatten[DDataC1], n];

DDataL1 = DataCy14[[2]][[All, 2]] - DataCy14[[1]][[All, 2]];
Do[DDataL1 = Join[{DDataL1, DataCy14[[i]][[All, 2]] - DataCy14[[i - 1]][[All, 2]]}], {i, 3, T - 1}]
DDataL2 = Partition[Flatten[DDataL1], n];

MDataL = Mod[DDataL2 + 1/2 H, H] - 1/2 H;
MData = Partition[
Partition[Riffle[Flatten[MDataC], Flatten[MDataL]], 2], n];

TTDataL = Table[1/(n) Total[Total[MDataL[[dT ;; t]]]^2], {t, dT + 1, T - 2}];
TTDataC = Table[1/(n) Total[Total[MDataC[[dT ;; t]]]^2], {t, dT + 1, T - 2}];
TTDataT = Table[1/(n) Total[Total[MDataC[[dT ;; t]]]^2 + Total[MDataL[[dT ;; t]]]^2], {t, dT + 1, T - 2}];
pL = ListPlot[TTDataL[[1 ;; 500]], PlotRange -> Full,
PlotStyle -> Blue];
pC = ListPlot[TTDataC[[1 ;; 500]], PlotRange -> Full,
PlotStyle -> Red];
pT = ListPlot[TTDataT[[1 ;; 500]], PlotRange -> Full,
PlotStyle -> Green];

rL = NonlinearModelFit[TTDataL, a \[Tau], a, \[Tau]];
rC = NonlinearModelFit[TTDataC, a \[Tau], a, \[Tau]];
rT = NonlinearModelFit[TTDataT, a \[Tau], a, \[Tau]];
A.3 Other results

In the figures below, the left graph shows the diffusion constant in the longitudinal (blue) and circumferential (red) direction for varying surface density. The right graph shows the ratio of the circumferential and longitudinal diffusion constant for varying surface density.

Figure 17: $\frac{R}{r} = 1$.

Figure 18: $\frac{R}{r} = 1.6$. 
Figure 19: $\frac{R}{r} = 2$.

Figure 20: $\frac{R}{r} = 10$. 