The Molecular Dynamic Simulation of neutral Argon Particles

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Bachelor of Science Thesis
(01-05-2007)

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Summary

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1 Introduction

Nano-particles are finding more and more applications in industry. For most applications nano-particles are required to have a narrow size distribution. This has proven to be a challenge for they grow at different rates and easily agglomerate. A novel technique is being developed to produce these particles using microwave plasma fields. The technique leads to the synthesis of nano-particles with a narrow size distribution. Each particle is given an equal charge which results in the particles repelling each other. This repulsion leads to a controlled growth of the particles and agglomeration is thwarted. In order to develop a better understanding of this behavior of these plasma fields, an attempt is made to numerically simulate the particles forming the plasma.

The first numerical simulation was carried out in 1953 when electronic computer became available for the first time. Where Metropolis et al conducted a simulation of dense liquids, thereby introducing the Monte Carlo (MC) method. A few years later in 1956 the first Molecular Dynamic (MD) simulation was reported. Since then computers have become readily available and many MD theories have been developed but the basic algorithms of these methods have not changed.

Numerical simulations form a bridge between laboratory experiments and the theory. To test the validity of a theory numerical simulations are performed, if the theory and the simulation do not agree it can be said that the theory is flawed. So by doing these simulations expensive laboratory experiments can be limited to when the theory is in agreement. With an increasing computational capacity larger and more accurate simulations can be conducted, thereby increasing their presents in the scientific world.

The simulations generate information at the microscopic level, which can be used to determine macroscopic properties, for example transport coefficients such as diffusion constants. Previous studies have used both MC and MD to determine the diffusion of low-density gas systems. A lot of this research is out dated due to the increased computer capabilities.

Using the MD neutral Argon particles where simulated. Argon was chosen for it is most favored gas used in plasma field studies. From these results a diffusion constant can be determined which can then be compared to the diffusion constant from the theory. At the conditions simulated the Chapman Enskog equation for the diffusion seems to be an adequate method for determining the diffusion constant. The system conditions where then varied to see whether the outcome would still be accurate. Parameters as temperature and density where varied along with some simulation parameters such as the number of particles. Different collision models where applied to see the effect on the outcome.

Once the limitations of the simulations are known further aspects can be included in the simulation such as adding positive charged particles or introducing electrons. The outcome of this research should give a better understanding of the plasma field behavior.

2 Theory

In order to setup a representative simulation and to be able to interpret the data generated from the MD simulations, the theory involved must first be carefully understood.

2.1 Molecular Simulations Techniques

There are two main types of molecular simulations techniques; Monte Carlo and Molecular Dynamics simulations in addition there are many combinations between the two methods, however they are not discussed in this report.

2.1.1 Monte Carlo

Monte Carlo (MC) simulations are based on determining the potential energy per location for different geometries. To describe the random walk process the Metropolis method is most commonly used, composed of the following steps.

1. Specify the initial coordinates of the system (r_i).
2. Choose a random atom i and move it with a random displacement (Δr_i).
3. Calculate the potential energy of the displacement (ΔU_i).
4. If $\Delta U_i < 0$ accept the new coordinates and go back tot 2.
5. Otherwise generate a random number R between 0 and 1 and

   if $\mathbf{exp}(-\Delta U_i / k_B T) < R$ accept the new coordinates and go back tot 2.

   if $\mathbf{exp}(-\Delta U_i / k_B T) \geq R$ keep the original coordinates and go back tot 2.

The simulation behaves as a so-called ‘Markov process’ meaning that each iteration is independent of another. The particles have no memory of its past, meaning that a transition to a future state depends only on its present state. Therefore the possibility of the system returning to its original state is just as likely as change to any other configuration. This probability is defined by the Boltzmann factor **(**$\mathbf{exp}(-\Delta U_i / k_B T)$). By calculating the potential energy for each configuration, certain thermodynamic properties can be determined.

2.1.2 Molecular Dynamics

Molecular Dynamics (MD) actually simulates what the atoms do as time progresses. The information generated from these simulations are a series snapshots taken at certain intervals (time steps). Based on the potential energy the acceleration can be calculated and thereby change is velocity is determined.

$$\vec{F}_i = \frac{\partial U_i}{\partial \vec{r}_i} = m_i \vec{a}_i \tag{2.1}$$

From particles position, velocity and acceleration the position and the velocity for the next time step can be calculated. Due to computational complexity of this method the amount of computer power required is quite substantial. To reduce computation time the system can be divided into several cells. One particle interacts with all the particles in the same cell as well as the surrounding cells as a whole. This method combines the particles in the surrounding cells to big pseudo-particles, thereby reducing the computer power required to calculate the potential energy of each particle. In the illustration below can be seen that the gray particle has to interact with much less particles by dividing the system into cells.

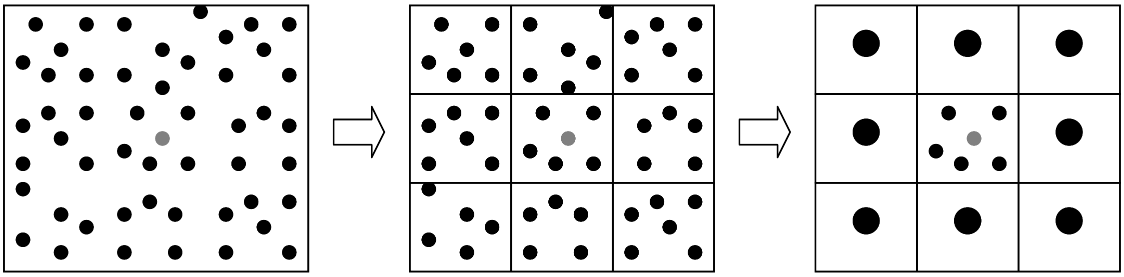

Figure 2.1: Illustration of the multiple cells method

Due to limiting computer capacity the amount of particles simulated is restricted, resulting in a system of a certain size. If the system size is sufficiently small boundary effects can influence calculations. To circumvent this problem ‘periodic boundary conditions’ have been developed, illustrated below. The system that is simulated is surrounded by identical images of it self, in other words the velocities and positions of the corresponding particles in the different boxes are identical. Visually this implies that when a particle leaves the system on the left it will enter the system again on the right. Using this approach a system of infinite size can be simulated.

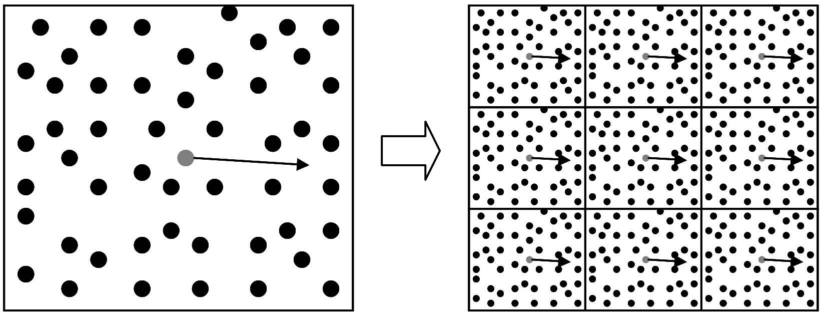

Figure 2.2: Illustration of the periodic boundaries principle

MD is a deterministic method of simulating and MC is a more stochastic method. Opinions on which method to apply in this case vary. MC simulations require much less computer capacity than MD simulations. As stated earlier the choice was made to use MD simulations for they will most probably give a more accurate result.

2.2 Kinetic Theory

A system of particles can initially be approximated using kinetic molecular theory. Of course this theory assumes that the particles behave as an ideal gas, but nonetheless it is a relatively accurate model to account for the velocity distribution and the mean fee paths of the particles. Kinetic theory describes the properties of gases by considering their composition and motion. This theory is only valid under the following assumptions:

- The gas consists of a large number of particles each with certain mass.
- The particles are in a state of constant random movement, obeying Newton’s laws of motion.
- The volume fraction of the system is very small, in other words the average distance between each of the particles is much larger than their radius.
- The energy of the particles depends solely on the temperature of the system.
- All collisions are fully elastic collisions, meaning that the kinetic energy after a collision is exactly the same as before the collision.
- All collisions are binary.
- All particles are in a state of ‘molecular chaos’ meaning that the velocities of colliding particles are uncorrelated, and independent of position.

Using these assumptions the velocity and the mean free path of the particles can be determined.

2.2.1 Velocity

Every particle has a velocity with a different magnitude and direction. In order to determine the velocity of the particles in the system a relation is found [lit.8], making the velocity temperature dependant.

$$PV = NkT \tag{2.2}$$

$$PV = \tfrac{2}{d} N \left\langle \tfrac{1}{2} m v^2 \right\rangle \tag{2.3}$$

$$T = \frac{2}{d k_B} \left\langle \tfrac{1}{2} m v^2 \right\rangle \tag{2.4}$$

$$\overline{U}_{kinetic} = \left\langle \tfrac{1}{2} m v^2 \right\rangle = \tfrac{d}{2} k_B T \tag{2.5}$$

This temperature is known as the kinetic temperature. The energy in this case is solely translational kinetic energy. The particles are assumed to be point masses and other degrees of freedom such as rotation and vibration have been neglected. From above equations the mean squared velocity in three dimensions is:

$$\left\langle v^2 \right\rangle = \frac{3 k_B T}{m} \tag{2.6}$$

In order to determine the velocity of each individual particle a Gaussian distribution of speed is used. This distribution is a result of the classical distribution function for energy.

$$f(U) = \frac{1}{A \exp(U / k_B T)} \tag{2.7}$$

Inserting the kinetic energy in this distribution and normalizing it results in a one-dimensional distribution of the velocity with an average velocity of zero.

$$f\left(v_x\right) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(\frac{-m {v_x}^2}{2 k_B T}\right) \tag{2.8}$$

When converting the distribution from Cartesian coordinates to spherical coordinates and integrating along the angles the Maxwell-Boltzmann distribution of speed is found.

$$f\left(v\right) = 4\pi \left[\frac{m}{2\pi k_B T}\right]^{\frac{3}{2}} v^2 \exp\left[\frac{-m v^2}{2 k_B T}\right] \tag{2.9}$$

From this distribution certain characteristic velocities can be calculated. These are the most probable, the average and the root-mean-square velocity respectively.

$$v_P = \sqrt{\frac{2k_BT}{m}} \tag{2.10}$$

$$\bar{v} = \sqrt{\frac{8k_BT}{\pi m}} \tag{2.11}$$

$$v_{rms} = \sqrt{\frac{3k_BT}{m}} \tag{2.12}$$

This distribution can be used to determine the particles initial velocity, realistically distributing their movement in different directions and speeds.

2.2.2 Mean free path

The average distance between collisions of two particles is known as the mean free path (λ). The maximum area around a particle in which a collision could take place is a sphere-shell with diameter ($2d$) this is the effective collision area.

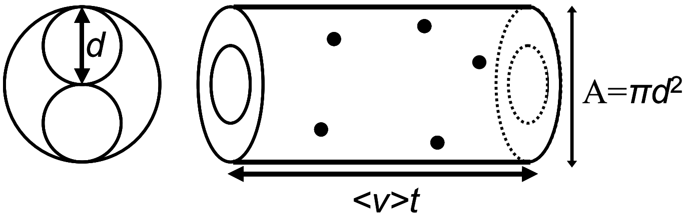

Figure 2.3: Mean free path illustration

This area will travel in time creating a tube shaped volume in which collisions will take place, thereby treating the target particle as a point mass. Now the mean free path can easily be calculated by taking the length of the path divided by the number of collisions.

$$\lambda = \frac{\bar{v}t}{\pi d^2 \bar{v}t \cdot n_v} = \frac{1}{\pi d^2 n_v} \tag{2.13}$$

The numerator is the distance travelled and the denominator is the interaction volume multiplied by the number density (n_v).

The above formula is inaccurate because the average molecular velocity is used thereby neglecting the fact that the target molecules are also moving. The frequencies of the collisions depend on the relative velocity of the particles defined below.

$$\overline{v_{rel}} = \sqrt{\overline{v_1}^2 + \overline{v_2}^2} = \sqrt{2}\bar{v} \tag{2.14}$$

The mean free path estimation thereby becomes:

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 n_v} \qquad (2.15)$$

The mean free path is useful in determining the simulation parameters such the time step, as will be described later.

2.3 Collision models

As explained before, during a collision all the kinetic energy is converted to potential and visa versa. This is illustrated in the plot below where a simple two particle collision is simulated. As can be seen the total energy remains constant thus complying with the energy conservation law.

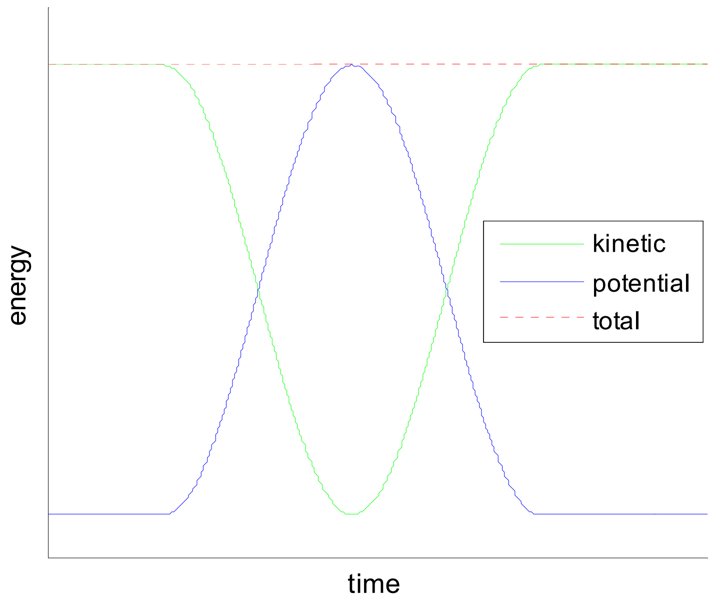

Figure 2.4: Energy vs time of a two particle collision

The collisions taking place between the particles can be described using several models depending on the particle properties. For the assumption that the particles experience hard sphere collisions the linear spring model is used, for long-range van der Waals interaction the Lennard Jones potential is applied and finally if there are charged particles present the Coulomb potential is used.

2.3.1 Linear spring

When assumed that the particles are hard spheres and there is no long-range interaction the only interaction will be the collisions of the particles. The particle collisions in this case are modelled by using a linear spring model. For instance two spheres approach each other and when the distance between each particle is less than zero the interaction follows the harmonic oscillation from the model in which the particles will overlap to a certain maximum and then repel each other.

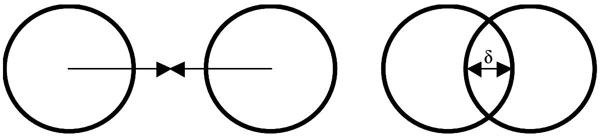

Figure 2.5: Linear spring collsion illustration

$$\delta(t) = (v_0 / \omega)\exp(-\eta t)\sin(\omega t) \tag{2.16}$$

In the harmonic oscillation the frequency is dependant on the spring constant *k*. The damping factor η is a result of the decreasing velocity.

$$\omega = \sqrt{\omega_0^{\ 2} - \eta^2} \tag{2.17}$$

$$\eta = v_{rel}(t)/(2m_{red}) \tag{2.18}$$

$$\omega_0 = \sqrt{k / m_{red}} \tag{2.19}$$

Where m_{red} is the reduced mass (particles with the same mass $m_{red} = m/2$) and v the relative velocity. The potential energy can of this harmonic oscillation be formulated as a function of the overlap or the distance of the center-mass of particle *i* from the center mass of particle *j*.

$$U_{spring} = \tfrac{1}{2}k\delta^2 = \tfrac{1}{2}k(a_i + a_j - r_{ij})^2 \tag{2.20}$$

As stated before δ can not be smaller than zero, this implies that the formula is only valid when $r_{ij} < (a_i + a_j)$. When $r_{ij} > (a_i + a_j)$ U_{spring} is set to zero.

2.3.2 Lennard Jones potential

The Lennard Jones potential (LJ) is a simple approximation of the van der Waals interaction where the particles at a certain distance *r* from each other are initially attracted towards each other and are then abruptly repelled. $1/r^{12}$ is the repulsion term and $1/r^6$ is the attraction term. ε is the depth of the well and σ is the separation at which $U_{LJ} = 0$ called the collision diameter. The values for ε and σ are tabulated for the different elements.

$$U_{LJ} = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\} \tag{2.21}$$

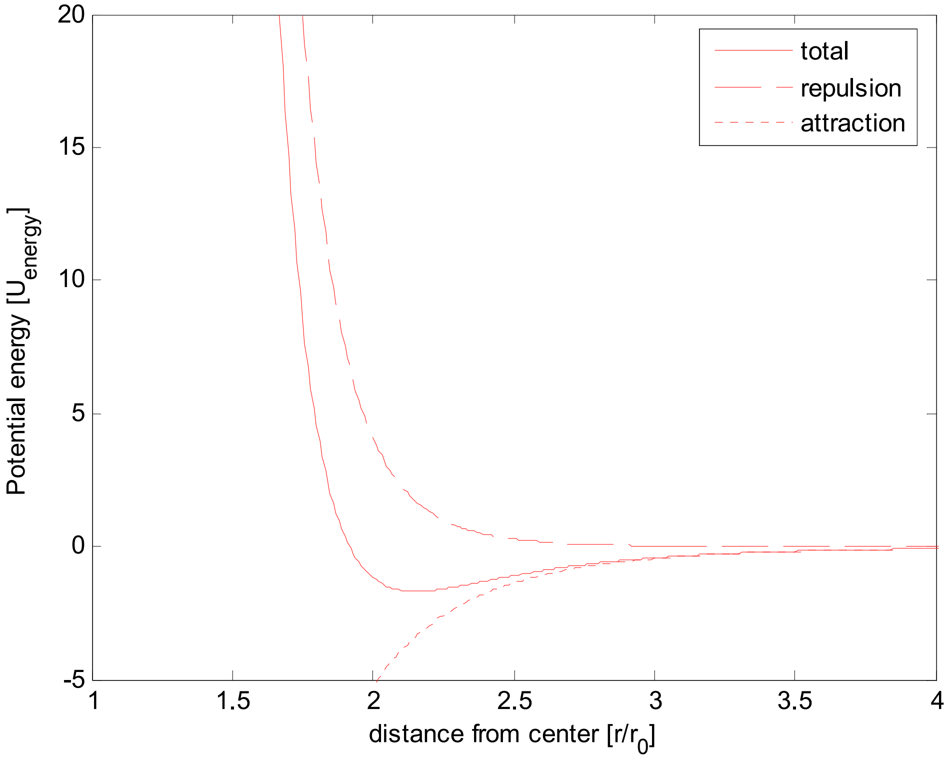

Figure 2.6: Lennard Jones potential as a function of the distance

2.3.3 Coulomb Potential

Coulomb's law states that particles of equal charge repel each other and particles of similar charge attract. Like point mass assumption in the kinetic theory described above the particles are assigned point charges. The potential energy of this repulsion or attraction force is expressed in equation(2.22). Where ε is the elementary charge ($1.602 \cdot 10^{-19}$ C), ε_0 is the electrical vacuum permittivity ($8.854 \cdot 10^{-12}$ C) and q the number and sign of the charge.

$$U_{Coulomb} = \frac{\varepsilon^2}{4\pi\varepsilon_0}\frac{q_1 q_2}{r} = k_{coulomb}\frac{q_1 q_2}{r} \tag{2.22}$$

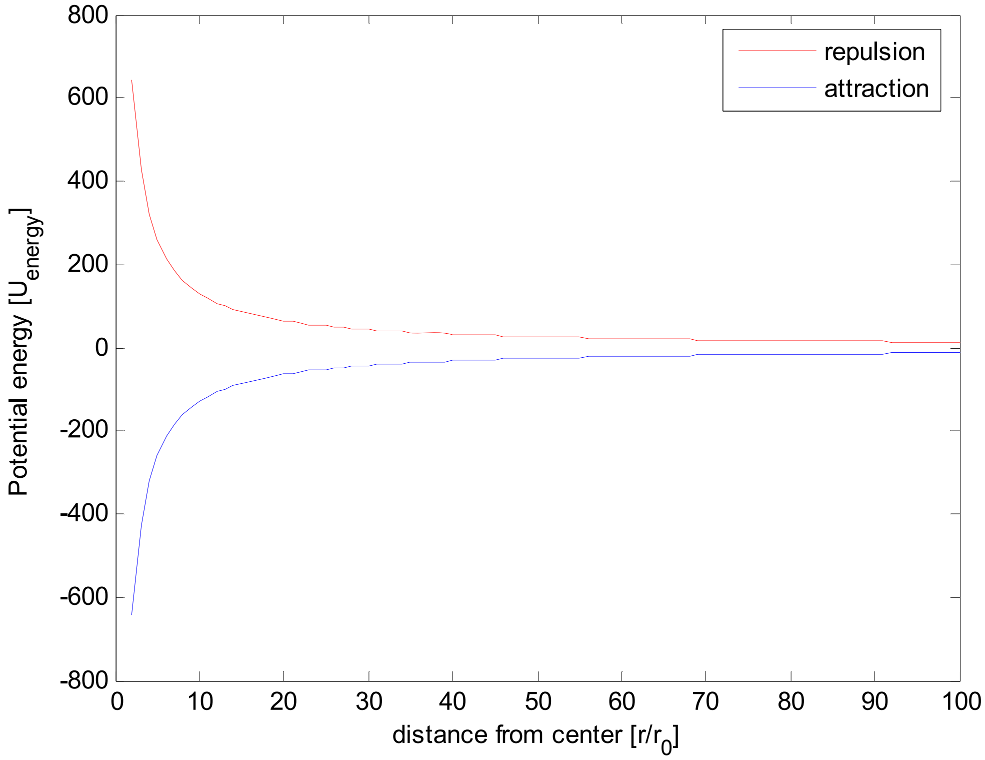

Figure 2.7: Coulomb potential as a function of the distance.

2.4 Diffusion

Diffusion describes the molecular transport of one substance relative to another because of their kinetic energy for random motion. In this case there is only one substance, so the diffusion is the molecular transport of the substance in itself, called self-diffusion. Chapman and Enskog have developed an equation that relates the self-diffusion to the kinetic temperature.

$$D = \frac{d\Gamma(d/2)}{4\pi^{\frac{d-1}{2}} n g_e \sigma^{d-1}} \left(\frac{k_B T}{m} \right)^{\frac{1}{2}} \tag{2.23}$$

Where d is the dimension n the number density (m^{-3}) and σ the diameter of the particles (m). g_e is the pair correlation function dependant on the volume fraction (ν) given below.

$$g_e = \frac{1 - \nu/2}{(1-\nu)^3} \tag{2.24}$$

Using the above equation the theoretical diffusion constant can be determined for different temperatures and densities. From the numerical simulations the diffusion constant can be determined using the correlation between the distance travelled and the diffusion.

$$r \propto \sqrt{Dt} \tag{2.25}$$

From literature an equation relating the diffusion constant to the mean squared of the distance travelled was found [lit. 6]. For the three dimensional case the diffusion in each direction is given by the function below.

$$\left\langle r^2 \right\rangle = 2Dt \tag{2.26}$$

3 Experimentation

Initially some simple experimentation was done in order understand the program. The next simulations that where conducted where to see what would happen if two particles would collided and to experiment with the calculation time steps in such a way that the output is still correct and that the total energy of the system remains constant (see Figure 2.4). After many attempts a working simulation was obtained for one thousand particles. The next step was to develop some Matlab code which could interpret the data the program gives as output. After lots of experimentation a proper simulation is run of which the results analyzed produce a realistic output. Of this simulation several variables can be varied to view the effect. The default settings are given in appendix BLA. From these settings only one parameter is varied each time keeping the rest constant.

3.1 The program

The simulation program developed by Stephan Luding was designed to simulate particles with various properties using the molecular dynamic model described above. The particles simulated where argon particles of which the properties required are tabulated below.

Table 3-1: Properties of Argon

Mass:	39.96	[g/mol]
Diameter:	3.58e-10	[m]
Lennard Jones parameters*:*		
ε:	6.760e-21	[J]
σ:	3.432e-10	[m]

The program can not handle values as small as the values presented in the table above, especially when converting the mass per mole to the mass per particle. So by manipulating the units to more sizable values the simulations could be conducted more accurately. In the table below the conversion factors are given.

Table 3-2: Conversion values for the units

Mass:	$1 \cdot 10^{-15}$	$[U_{mass}/kg]$
Length:	$1 \cdot 10^{-6}$	$[U_{length}/m]$
Time:	$1 \cdot 10^{-3}$	$[U_{time}/s]$

All the settings required for the program are placed in ini-files. Each file has its own purpose. The table below shows what is specified in each ini-file. For the most basic simulations only a par.ini and a c3d.ini are required.

Table 3-3: The ini-files for the MD program

Par.ini	Time specifications, spring constant and particle density
C3d.ini	System size, particle location, velocities and radius
Lcell.ini	Number of cells in each direction (x,y,z)
Species.ini	Particle properties (e.g. particle density)
Specnum.ini	Associating particle numbers (c3d.ini) with the particle properties (species.ini, longrange.ini)
Longrange.ini	Long-range interaction properties.

A lot of the inter-particle effects where not included in the simulation and where therefore set to zero in the ini-files (eg. rotation, vibration). Once the ini-files have been specified the simulation can be started. The program does not just produce the output required for the further calculations but also on its progress and the parameters it has loaded from the ini-files. This is saved to a file, making it easier to trace errors when they occur. A set of ini-files is presented in appendix BLA, these ini-files correspond to the simulation run using the default settings.

3.2 Simulation setup

In creating a simulation several criteria have to be met in order for the simulation to be realistic, but also to prevent the simulation from crashing. What is done when setting up a simulation is; several particles are given random location and velocities in a defined system space. When the simulation starts the particles will start to move and interact with each other, where an output is given per specified time step of each particles location. All the inputs that are needed to start a successful simulation are described below.

3.2.1 Input parameters

The main parameters required for a representative simulation are the volume fraction and the temperature of the system and the number of particles to be simulated. These parameters have to be chosen in a manner that will result in a simulation with a realistic output.

Volume fraction

The volume fraction (v) should be chosen sufficiently low for the kinetic theory described above to be applicable. If not, results will deviate from theory.

$$v = \frac{N\left(\frac{4}{3}\pi r^3\right)}{l^3} \tag{3.1}$$

Temperature

The temperature (T) can be chosen freely, although the higher the temperature the more excited the particles are and the higher there velocities will be. High velocities result in small simulation time steps as will be discussed below which will lead to long computation times.

Number of particles

The number of particles (N) influences the accuracy of the simulation. More particles results in a less scattering of the data and a larger the reproducibility. But more particles also mean more calculations, therefore longer computation times. A value should be chosen that leads to acceptable computation times as well sufficient reproducibility.

System size

The system size influences several other factors in the simulation, but for a representative simulation, it is important that several collisions take place before the particles cross the system boundary. Otherwise the particles might travel several times across the system before a single collision has taken place. This results in an unrealistic simulation and will lead to faulty diffusion calculations. So the length of the system should at least be larger than mean free path.

$$l >> \lambda \tag{3.2}$$

The system size is however not an independent variable. It depends on the chosen volume fraction and the number of particles. So when these two values lead to a system which is not large enough for several collisions to take place these values should be adjusted.

Time step of the Output

The time step of the output must be chosen small enough so that there are several outputs before the particles cross the system. Otherwise it is not possible to tell if the particle jumped from left to right or from right to left when they cross the system boundary.

$$\Delta t_{output} << \frac{l}{\bar{v}} \tag{3.3}$$

Time step of the calculations

The time step of the calculation (Δt) must be smaller than the collision time (t_c) otherwise the particle-particle interaction is not calculated frequently enough and particles might suddenly be occupying the same space at the same time. When this happens the repulsive energy repels the particles with such great force that the speed of these particles will increase considerably and thereby increasing the total energy of the system, which is of course physically incorrect.

$$t_c >> \Delta t \tag{3.4}$$

3.2.2 Collision time

The collision time is the moment from which a particle starts to decelerates towards another particle until the moment where the particle stops accelerating away from that particle. The kinetic energy is converted to potential energy which is then converted back to kinetic energy. The collision time depends greatly on the collision model used.

Linear spring

When the interaction between the particles is simulated using the linear spring model, the collision time is determined by assuming a frontal collision, a collision where all the kinetic energy is converted to potential energy and back again. In the case of the linear spring model this results in a so called maximum overlap (δ_{max}).

$$\delta_{\max} = v_{rel}\sqrt{\frac{m_{red}}{k}} \tag{3.5}$$

The collision time can no easily calculated by dividing the maximum overlap by the relative velocity;

$$t_c = \frac{\delta_{\max}}{v_{rel}} = \sqrt{\frac{m_{red}}{k}} \tag{3.6}$$

The collision time, as can be seen, is determined by the spring constant. So when only using a linear spring the spring constant can be varied along with the time step to reduce computation time.

There is however a limit to how small the spring constant can be, for the maximum overlap should always be much larger than the radius of the particle. So the choice in spring constant is on one hand limited by the time step and on the other hand by the radius of the particle.

$$t_c >> \Delta t \tag{3.4}$$

$$a >> \delta_{\max} \tag{3.7}$$

Lennard Jones

To estimate a collision time for this type if interaction a function for the ‘LJ constant’ is calculated which can be inserted in equation(3.6). When taking the second derivative of the linear spring model one is only left with k. So by taking the second derivative of the LJ potential a function is found for the ‘LJ constant’.

$$\frac{\partial^2 U_{spring}}{\partial r^2} = k \tag{3.8}$$

$$\frac{\partial^2 U_{LJ}}{\partial r^2} = 4\varepsilon\left[156\frac{\sigma^{12}}{r^{14}} - 42\frac{\sigma^6}{r^8}\right] = k_{LJ} \tag{3.9}$$

The value of *r* that should be used in this equation is determined from the point at which all the kinetic energy is converted to potential energy. Resulting in the collision time below.

$$t_c = \sqrt{\frac{m_{red}}{k_{LJ}}} \tag{3.10}$$

Coulomb Potential

The same approach can be used for the coulomb potential, resulting in a 'CP constant'.

$$\frac{\partial^2 U_{Coulomb}}{\partial r^2} = \frac{2kq_1q_2}{r^3} = k_{CP} \tag{3.11}$$

When using longrange interaction like the Lennard Jones potential or the Coulomb potential, a cut-off radius must be specified in order to limit the amount of calculations. At a chosen distances these potentials are then set to zero. These distances are chosen arbitrarily. Once the collision time is known a proper time step can be chosen. Choosing an appropriate calculation time step is critical. Too large time steps errors can occur resulting in the increase or decrease of the total amount of energy in the system. On the other hand too small time steps will cause exceedingly long computation times.

3.2.3 Particle initial conditions

The particle starting situation must be defined. This is done by assigning each particle a location and a velocity in a certain direction. Certain other properties also have to be defined such as radius, density and interaction parameters.

Initial Location

Distributing the particles over a certain space has some complications. Firstly the particles should not overlap each other and secondly there can be no drift.

Generating random locations without overlap is done by creating more random particles than specified and just removing the particles that overlap others and then removing the surplus particles to the amount specified. To see if a particle overlaps another, the distance between the particles is calculated which should be larger than twice the radius of the particle, if not the particle is removed.

$$r > 2\sigma \tag{3.12}$$

When working at high volume fractions (larger than 20%) this method is not very efficient. The probability that particles will overlap is quite large and by creating more particles as described above this probability is increased further. In this case the particles are assigned positions on a 3 dimensional lattice so that they will be equidistant from each other.

Initial velocity

The second problem is the velocity. The velocity of each particle was initially determined by the temperature according to the average particle velocity from the Maxwell distribution of speed equation (2.11). The particle direction was generated randomly so that the average velocity over all the particles was zero.

$$\bar{v} = \left(\frac{8k_bT}{\pi m}\right)^{0.5} \tag{3.13}$$

This is unfortunately not an accurate model of reality, a better approach was to use a Gaussian distribution in each direction with the standard deviation of $\sigma = k_BT/m$, resulting in a 3 dimensional Maxwell-Boltzmann velocity distribution with an average velocity of zero. A cut-off was defined in order not to have ultra fast particles, which could lead to simulation problems. The cut-off was set to twice the standard deviation thereby removing approximately the fastest 5% of the particles. After generating this distribution the average velocity is still not exactly zero and therefore drift is present in the system. Drift has to be removed for it will influence the diffusion calculations. Since the direction of the velocity is purely random, calculating the average velocity in each direction and subtracting it from each velocity component removes the drift.

$$\vec{v}_i = \vec{v}_i - \langle \vec{v} \rangle \tag{3.14}$$

Now two manipulations have been done to the original set of velocities: removing the fastest 5% and removing the drift. These manipulations have resulted in a decrease of the total energy in the system. Without correction no comparison will be found with the theory. The correction factor applied to the velocities is the ratio between the theoretical root mean squared velocity and the actual root mean square velocity.

$$v_i = v_i \cdot \left(\frac{\overline{v^2}_{theoretical}}{\overline{v^2}}\right)^{0.5} = v_i \cdot \left(\frac{3k_BT}{m\overline{v^2}}\right)^{0.5} \tag{3.15}$$

After all these computations a set of particles with random locations and velocity is obtained.

All the specifications needed for a simulation are generated by Matlab programs using the equations above. The program code is given in appendix BLA. All one needs to do is input the parameters. A check is then preformed to verify if these parameters conform to the limitations and restrictions described above. The Matlab program then generates the ini-files needed and an information file giving the settings as well as several calculated values useful for evaluating the results and tracing errors (e.g. the mean free path and the collision time). The parameters which need to be specified are listed below.

Table 3-4: Paramters needed to setup a simulation

Time step of the calculations	
Time step of the output	
Temperature	
Number of particles	
Volume fraction	
Longrange forces	*(yes or no)*
The spring constant	*(when using the linear spring otherwise 0)*
The cut-off radii	*(when using longrange forces)*

3.3 Evaluating the simulation output

Firstly, before the results generated can be used to determine the diffusion constant it is necessary to see if the energy of the system of particles remains constant during the entire simulation. Once this is the case the diffusion constant can be calculated.

3.3.1 Energy balance validation

For each output time step the total potential and kinetic energies of the particles is reported. The sum of these values should remain constant during the entire simulation.

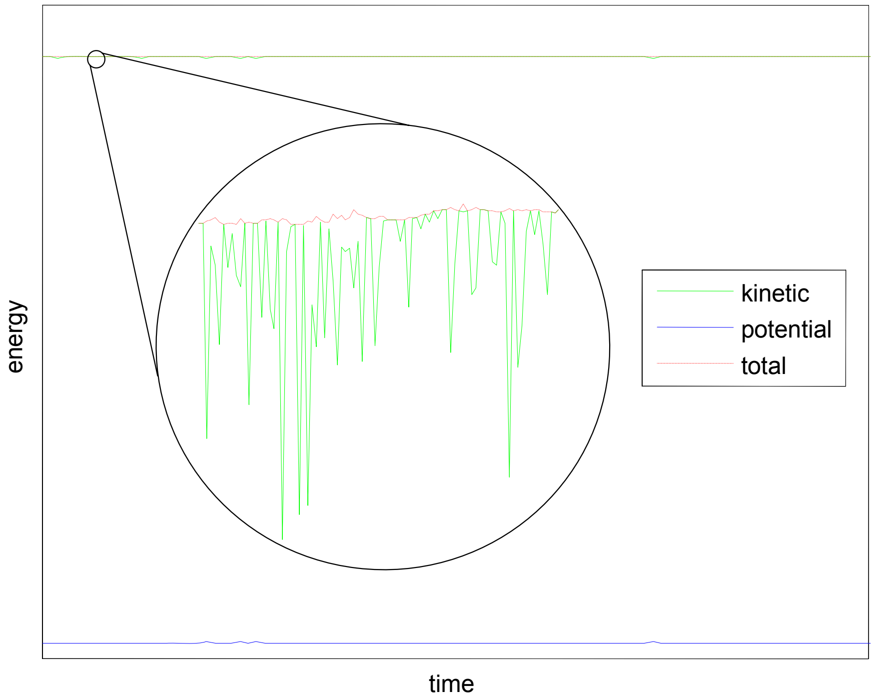

Figure 3.1: Energy plot, illustrating the energy fluctuations in time.

In this plot the deviations in the total energy can be observed, but the average total energy over time remains more or less constant. Some minor deviations are usually observed, but these are due to numerical errors and as long as there is no major change in the total energy over time the results can be used for further calculation.

3.3.2 Diffusion calculation

The program gives the location of all the simulated particles per output time step. From this information the mean squared distance travelled can be calculated needed to determine the diffusion constant as explained above. The mean square distance is the average of the square distance of every particle from it's origin per time step.

$$\left\langle r^2 \right\rangle(t) = \frac{\sum_i^N (r_{i,0} - r_{i,t})^2}{N} \tag{3.16}$$

Since in the simulation periodic boundaries where used it is difficult to calculated the distance to the origin for then the distance will never be larger than the system size. So instead the distance travelled between each time step was calculated and then summed to get the distance from the origin.

$$\left\langle r^2 \right\rangle(t) = \frac{\sum_i^N \left(\sum_0^t \Delta r_{i,t} \right)^2}{N} = \frac{\sum_i^N \left(\sum_0^t (r_{i,t+\Delta t} - r_{i,t}) \right)^2}{N} \tag{3.17}$$

Another problem is the fact that particles can leave the system on one side and enter on the other. It will seem like the particles have travelled across the system in just one time step, having a sudden increase in velocity. To eliminate this problem, the particles that travel more than half the system length in one time step will be subjected to a correction. The correction depends on the direction in which the particles travel. If the particles leave the system on the left and enter on the right, it will seem like they have travel in a negative direction. So in this case by adding the length of the system this problem will be corrected and visa versa for particles leaving from the right.

$$\Delta r_{left-right} = r_{t+\Delta t} - r_t + l \tag{3.18}$$

$$\Delta r_{right-left} = r_{t+\Delta t} - r_t - l \tag{3.19}$$

The diffusion constant can now be determined by fitting equation (2.26) to the data.

$$D = \frac{\left\langle r^2 \right\rangle}{2t} \tag{3.20}$$

By plotting the diffusion constant versus time in a logarithmic plot the different stages of diffusive behaviour can be seen. Initially the system is in the ballistic regime but after some time diffusion remains constant, meaning that diffusion limitation is reached. The time needed to reach the diffusion limited regime is known as the settling time, this is illustrated in the plot below.

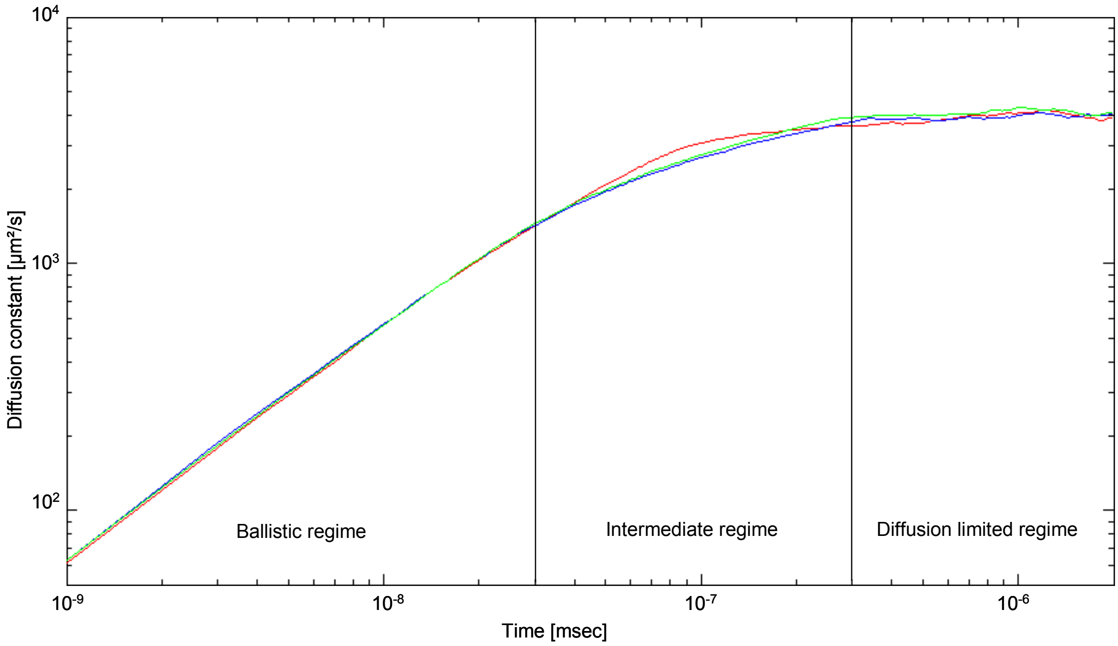

Figure 3.2: Log-log plot of the diffusion constant versus time.

Once again all the calculations that are done after a simulation has been completed are performed in Matlab. The program code can be found in appendix BLA. The diffusion constant of the system in the diffusion limited regime is calculated by taking the average diffusion from the moment the plot becomes more or less horizontal. So for every simulation one diffusion constant can be determined and compared to the Chapman Enskog diffusion constant.

4 Results

Many different simulations where conducted using the default settings and varing only one parameter each time.. The purpose was to see what the effect is of several parameters on the diffusion constant. As mentioned earlier the volume fraction, temperature, number of particles and the different collision models where investigated. For various values of these parameters the diffusion constant wass compared the Chapman Enskog diffusion constant.

4.1 Volume fraction

Simulations where conducted, varying only the volume fraction, the rest of the parameters where kept constant. The diffusion constant was determined for each volume fraction. The plot below shows the results of the simulations, the solid line represents the Chapman Enskog diffusion from equation(2.23).

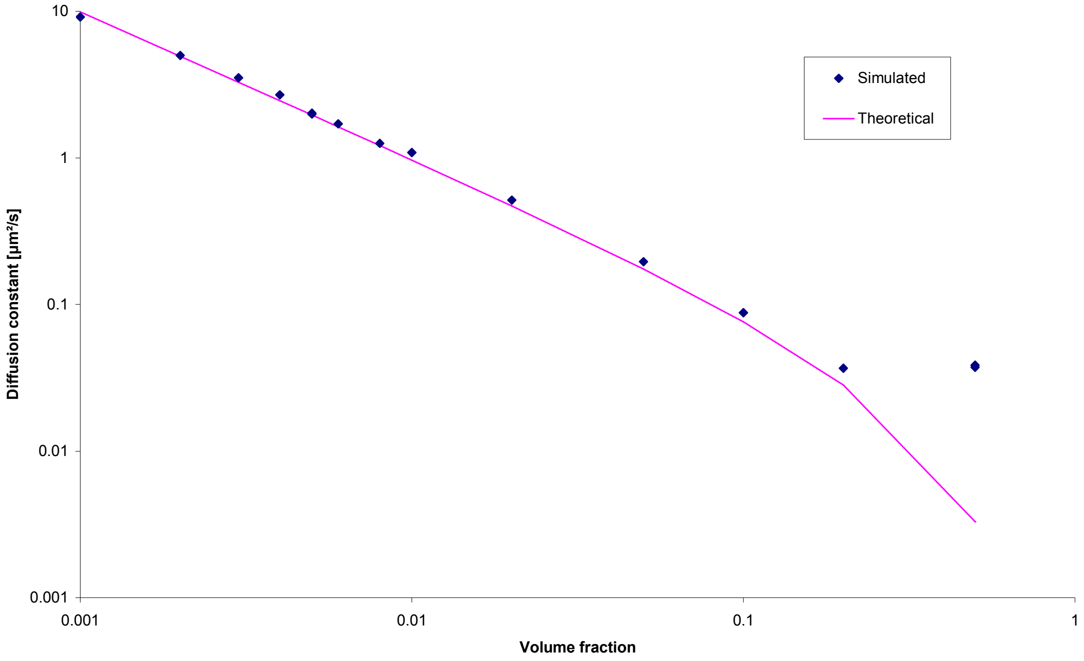

Figure 4.1: The diffusion constant as a function of the volume fraction

It is clear from the plot, that the lower the volume fraction is the smaller the relative deviation of the diffusion constant from the theoretical will be. This is true because for the lower the volume fraction the more compliance there is with the kinetic theory from which the theoretical diffusion is determined. The mean free path also becomes larger at lower volume fraction and therefore collisions are less frequent. This results in a longer settling time which then implies longer simulation times. In Appendix bla a few diffusion plots are given.

4.2 Temperature

As explained above the temperature has a direct influence on the velocity of the particles in the system. The higher the temperature the faster the particles will move. So for the simulations this implies; the higher the temperature the shorter the collision time and therefore the smaller the time step of the calculation has to be. The temperature was varied from 100K to 1000K with and increment of 100K. The plot below shows the simulated diffusion constant as well as the theoretical diffusion constant for each temperature.

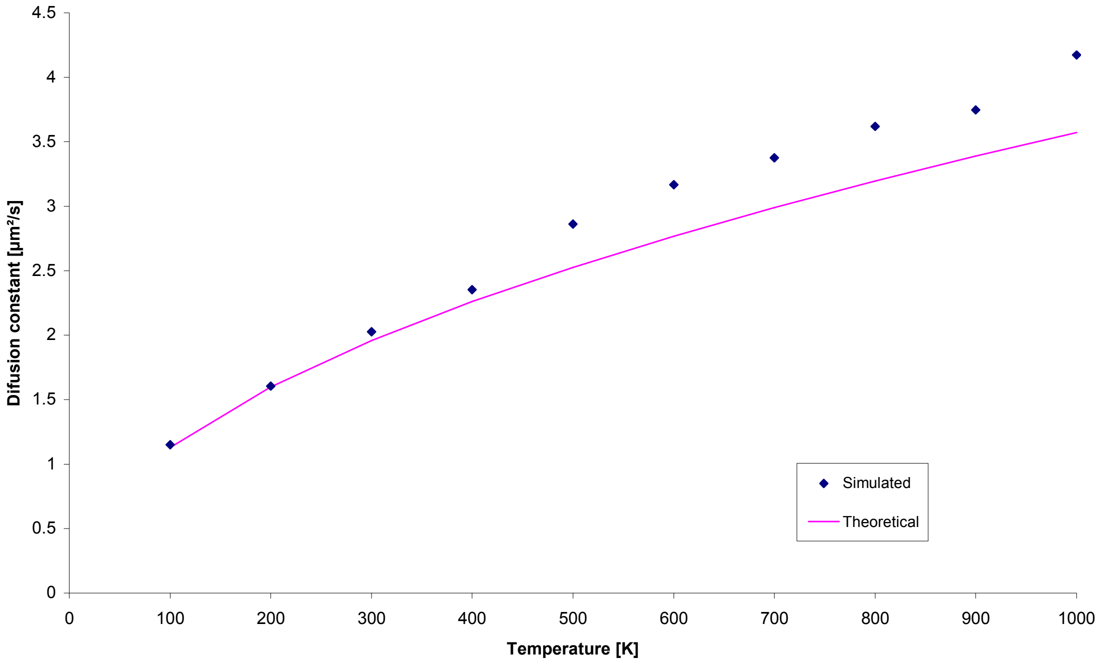

Figure 4.2: Temperature dependence of the diffusion constant

As can be seen at increasing temperature the simulated diffusion constant deviates more from the theoretical. An explanation is the short collision times at high temperature resulting in inaccurate calculations because the time step is kept constant in each simulation. Another phenomenon which is observed is a decrease in settling time at higher temperatures. This is of course due to the increasing velocity. Looking solely at the calculation time, high temperatures causes short settling times but small time steps and visa versa for low temperature. The settling time decreases at a much lower rate than the time step has to be reduced. This Means that the higher the temperature the longer the calculation time.

4.3 Number of particles

To see what the influence is of the amount of particles several simulations have been done, each with a larger set of particles. The plot below clearly shows that with an increased amount of particles the scattering of the data is less.

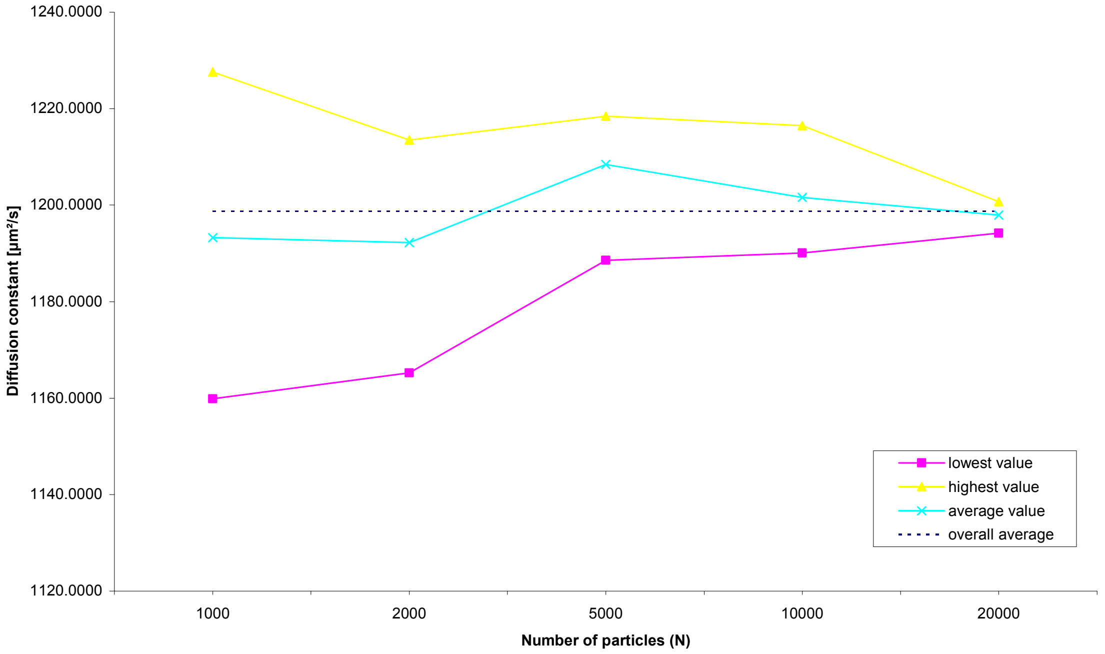

Figure 4.3: The diffusion constant as a function of the number of particles

The more particles simulated, the larger the system size will be at constant volume fraction. Therefore the wall effects will be less when using more particles. The only problem is that with a large number of particles the computation time increases drastically. More particles mean more interactions and therefore more calculations but more accuracy.

4.4 Collision models

The different collision models explained in the theory are used individually and in combination. Some experiment where conducted to see the influence of spring constant on the diffusion. The Lennard Jones potential was applied individually and in combination with the linear spring too see which best represents the actual behaviour of the particles. When using the coulomb optional several problems where encountered, as will be explained below.

4.4.1 Linear Spring model

The spring constant was varied to see which value best coincides with the theoretical diffusion. As explained above the spring constant is has a lower limit, for the maximum overlap must be smaller that the radius (equation (3.7)), and an upper limit, the collision time larger then the time step of the simulation (equation (3.4)).

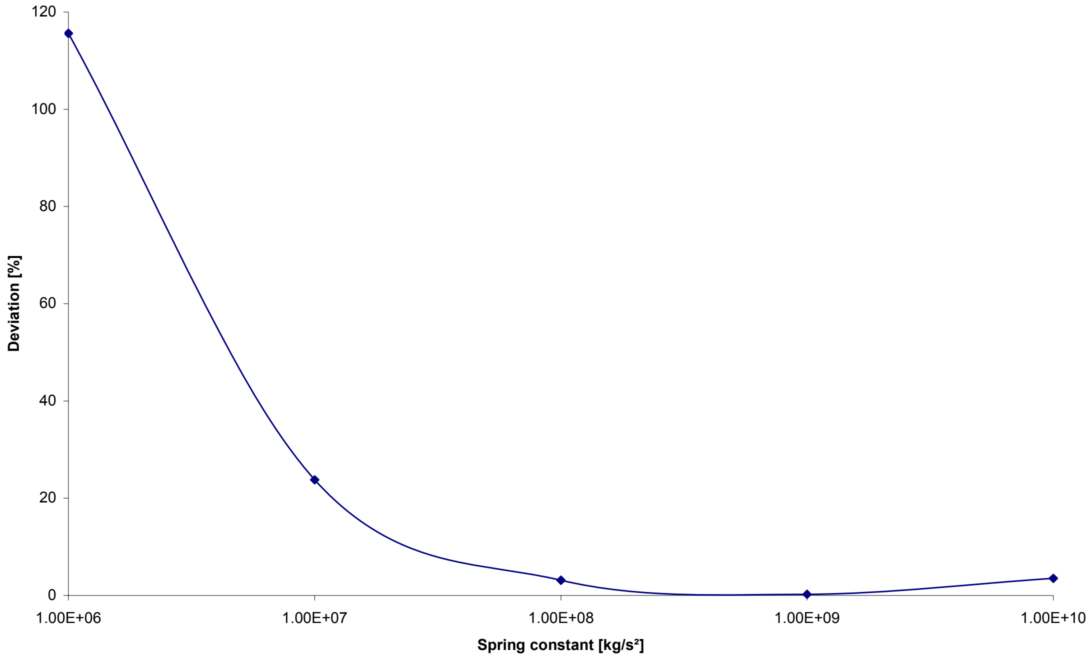

Figure 4.4: The deviation of the diffusion constant from the theory at various spring constants

The plot above clearly shows an optimum at a spring constant of $1 \cdot 10^9$ kg/s^2. The spring constant directly influences the time step needed for calculations. A favourable time step would be a small one, but unfortunately this does not give the best result. However in the default settings for the simulations conducted a spring constant of $1 \cdot 10^8$ $1 \cdot 10^9$ kg/s^2 is used in order to reduce computational time and still have a relatively accurate output.

4.4.2 Lennard Jones potential

Several simulations where conducted; one without LJ-potential, several with LJ-potential and one with only the LJ-potential. The simulations with the LJ-potential where conducted several times with varying cutoff radius. The cutoff radius of the LJ potential is defined as a multiple of the radii of the two particles involved in the collision, meaning that the LJ_{cutoff} has to be specified in the ini-files.

$$r_{cutoff} = LJ_{cutoff} \cdot (a_1 + a_2) \tag{4.1}$$

When a cutoff radius of one is chosen, the LJ potential is cutoff at the distance at which the particles touch each other. The diffusion constant from this simulation is no different from the simulation with only the spring constant. The reason is that the linear spring model will overrule the LJ potential at this distance. This is illustrated in the energy plot below.

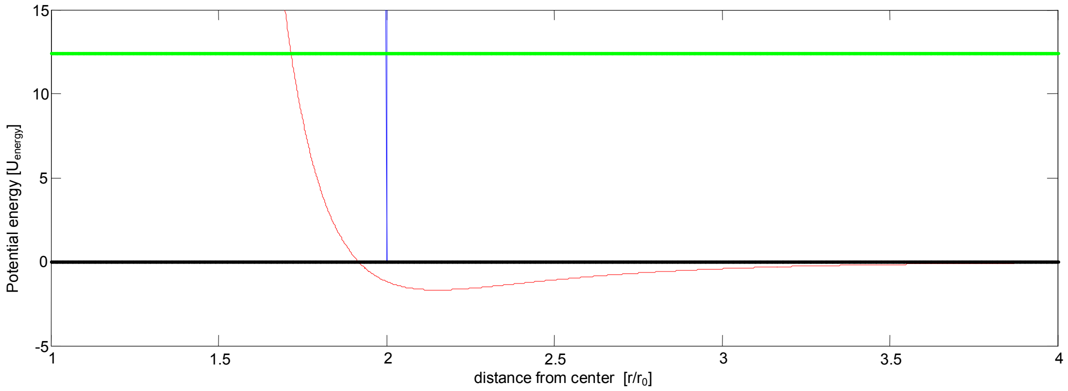

Figure 4.5: Energy plot as a function of the distance between two particles' centre mass. The green line shows the total energy of the system, the blue line the potential enrgy plot as a result of the linear spring and the red line is the Lennard Jones potential.

When conducting a simulation without the linear spring model no diffusion limitation is found. The particles stay in the ballistic regime and the diffusion increases linearly in time. When the particles start to deform as a result of a collision the LJ potential does not accurately calculate the potential energy and therefore the linear spring is needed at this distance. In the later experiments both interaction where used and the cut-off radius of the LJ potential was varied. The results from these experiments are presented in the table below.

Table 4-1: Diffusion constants calculated from simulation including the LJ potential at different cut-off radii.

Cutoff radius (LJ_{cutoff})	Average diffusion constant [μm²/s]	Standard deviation [μm²/s]
No LJ	2152	104
1.5	2051	31
2.0	2073	102
4.0	2001	110

The diffusion constant changes at different cutoff radii. An explanation is that the scattering of the data is larger at an increased cutoff radius resulting a more widely spread diffusion constant. As can be seen in the table at a cutoff radius of 1.5 a relatively low standard deviation is found. The value of the diffusion constant at this cutoff radius is also closer to the theoretical self-diffusion constant (1957 μm²/s). Unfortunately calculations are greatly complicated when applying the LJ potential and cause simulations to take exceedingly long.

4.4.3 Coulomb potential

When simulating charged particles, the coulomb potential is used. The problem however with this potential is that the radius at which it has and influence is extremely large. So a very large system has to be used and a very small calculation time step. This results in long and tedious simulations for which the computational power required is quite substantial. These simulations where attempted but aborted due to the limiting computer power available.

The plots below show the three collision models used. The solid green line is the total energy of the system. The potential energy resulting from the collision models cannot exceed this value. As can be seen from the plot below the radius at which the coulomb potential has reached this value is at an enormous radius (>100). This implies that the 'radius' of a charged particles, or the closest two particles of equal charge can approach each other is over a hundred times their radius. The opposite is of course true for particles of different charge. They accelerate towards each other at an enormous rate leading to very high velocities requiring very small calculation time-steps for accurate results.

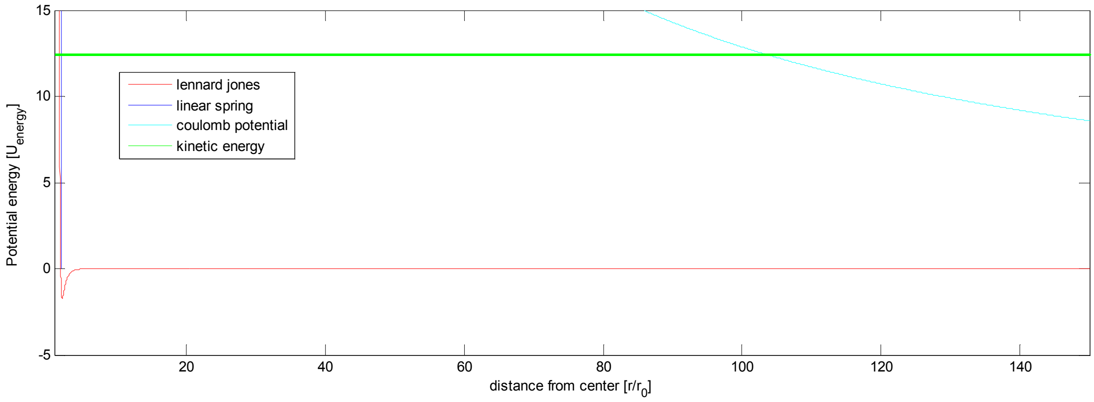

Figure 4.6: The three collision models' potential energy plotted vs. the distance between the particles' centre mass. The green line shows the total energy of the system, the blue line the potential enrgy plot as a result of the linear spring, the red line is the Lennard Jones potential and magenta line the Coulomb potential.

The time steps required to perform these calculations are so small that simulations would take weeks and therefore the Coulomb potential was not simulated.

4.5 Number of cells

The number of cells is a method to reduce the amount of calculations as explained previously. The problem however is that the interaction range of the particles should fall inside one cell otherwise a distorted interaction is calculated. Some experimentation was done for various amounts of cells. The plot below shows the simulation results. The only thing which was varied was the amount of cells the rest was kept constant.

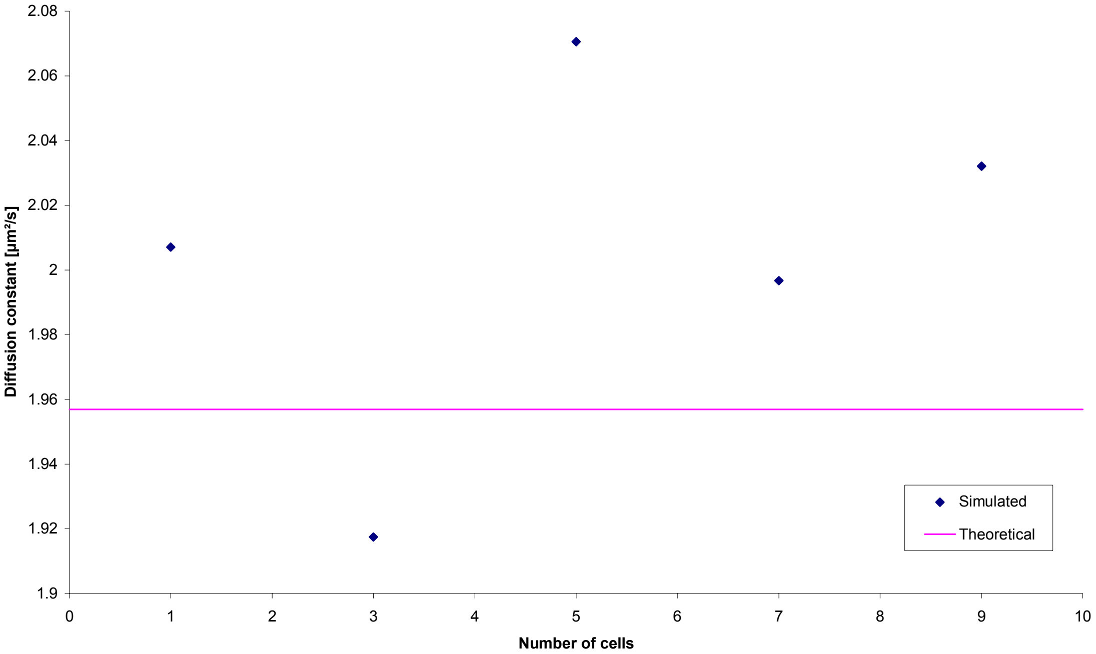

Figure 4.7: Number of linked cells vs. the diffusion constant

As can be seen no relation can be seen between the amount of cells and the deviation from the theoretical diffusion. Of course if more simulations where to be conducted at an increasing amount of cells at some point a limit will be found. Another problem with using more cells, every time a particle leaves a cell and moves to another, the system has to resort the linked cells resulting in extra computation time. So there is an optimum some where between the amount of linked cells used and the computation time, which was not determined is this project.

5 Conclusion and recommendations

From almost all the simulations conducted it can be concluded that settings which result in longer computation time result in better comparison with the theory. Also the closer the simulated system resembles an ideal gas the close the calculated diffusion constant is to the theory. For the two collision models used, linear spring and the Lennard Jones potential, an optimal value is found for the parameters varied in each case. For the Lennard Jones potential one would expect that the larger the cut-off radius the more accurate the calculations are. The situation as seen in the results is that at short cut-off radii the scattering of the data is less. Also using the Lennard Jones potential together with the linear spring model, result in a better comparison with the theoretical self-diffusion constant.

The main problem with all the simulations conducted is the time needed to do them. The average computation time is roughly half a day. Therefore less simulations where conducted than preferred. There are also many variables which influence the outcome of the simulations. For example, it might be that finding an optimum for the spring constant is different when using different time steps. This would have to be confirmed.

An option is to use the Monte Carlo method instead of the Molecular Dynamic method for it requires much less computer power. However the question still remains if it is as accurate but this can then be proven. Another alternative is to simple use more powerful computers making it possible to conduct faster and more accurate simulations.

A more complicated option is to use random forces at certain intervals thereby mimicking collisions and making it possible to use larger time steps. A problem however when applying these forces is that the total energy of the system is influenced and care has to be taken to assure that the total energy remains constant.

Once the diffusion constant can be determined using these simulations, the next step would be to develop a new diffusion theory for the situation when there are also charged particles present. This theory can then be verified using simulations. Although when using charged particles very low densities have to be used and considerable computer power is required. Simulating electrons will prove even more difficult for they move a lot faster than the other particles. An option is then to assume that the other particles are not moving and assigning unique location to each and just simulating the electrons. Again here it might be a good idea to use random forces.

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