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Brownian motion

1   Diffusion and Brownian motion

Diffusion is the movement of particles from a higher to a lower density [1]. It can be used to describe the mixing of two substances of different temperature or composition. Because diffusion is fairly complicated, we use Brownian motion in the simulation, which can be considered as a probabilistic model for diffusion and it is much simpler to implement [2].
Brownian motion is the result of thermal motion and considered a completely random movement of the particles.

2   Theory

2.1   Brownian motion

Displacements of a Brownian particle can be defined via Einstein s approach by considering a particle which diffuses for t amount of time. In this time it has diffused x amount from the starting position either to the left or right with equal probability if there are no outside forces. So, the average placement of all particles is 0. Because all of the particles exist in the pipe, we can define the probability density function as (1) [3]. In the function P(x,t) is the probability of finding the particle after time t.

$$\int_{-\infty}^{\infty} P(x,t)dx = 1$$

The concentration can also be written as the solutes diffusion equation in then given dimension. Where $\rho(x, t)$ is the probability to find the particle at position x.

$$\frac{\partial}{\partial t}\rho(x, t) = D\frac{\partial^2}{\partial x^2}P(x, t) \tag{1}$$

We can rewrite the above equation by substituting the yeilds for the probability function.

$$\frac{\partial}{\partial t}P(x, t) = D\frac{\partial^2}{\partial x^2}P(x, t) \tag{2}$$

Using integration over the entire system we can figure out the displacement.

$$< x^2 >= \int_{-\infty}^{\infty} P(x, t)x^2 dx \tag{3}$$

Then we can take a time derivate of the equation and replace the term on the right side with equation 3.

$$\frac{d}{dt} < x^2 >= \int_{-\infty}^{\infty} \frac{\partial}{\partial t}P(x, t)x^2 dx = \int_{-\infty}^{\infty} D\frac{\partial}{\partial x^2}P(x, t)x^2 dx \tag{4}$$

P(x,t) shape must resemble a bell curve. Since the particle is equally likely to go to either direction the probabilities because of P(x,t)=P(-x,t). With the given limits x$\pm\infty$ and moving away from origin p(x,t), and its first and second derivates will all monotonically approach zero. Integrating the function (4) produces the average displacement due to Brownian motion(5)[3].

$$(< \bar{x}^2 >) = 2Dt \tag{5}$$

In the formula (5) D is the diffusion coefficient of the material and t is the amount of time. x is the average displacement travelled in one dimension during the time t. Because we are dealing with a two-dimensional system we need to do the calculation for both x and y coordinates separately. We

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can derive the effective speed of the particles in each dimension by taking a derivate of the displacement [3].

$$v_{eff} = \frac{d\sqrt{<x^2>}}{dt} = \sqrt{\frac{D}{2t}}$$

This is done for the y coordinate the same way. Effective speed is only a valid method of modelling diffusion if the time scale is much larger momentum relaxation time. So, in this simulation, we can use effective speed sense the simulation time is at least 7 to 9 magnitudes bigger [3]. Effective velocity was used to calculate the mean displacement for every step and then combine them to get the displacement at point t for each particle separately. This way we can see the evolution of the system.

$$<x>^2 = \sum_{i=0}^{j} <x_i>^2 = \sum_{i=0}^{j} \int_{t_i}^{t_{i+1}} v_{eff} dt$$

2.2   Diffusion coefficient

Each substance has its own diffusion coefficient and depends on the properties of the substance. There are many ways calculating the coefficient, depending on its properties, for fluids we can either use the Stokes-Einstein or Wilke-Chang equation for example [4].

Stokes-Einstein is used for bigger particles where the surrounding liquid can be considered a continuum. Wilke-chang is used for small particles. Even though the model's particle size is could be considered small or non-existent the equation used was the Stokes-Einstein because it is much simpler due to it not requiring the info about the solutes and solvents interaction or molar volume. Stokes-Einstein is not the most accurate equation for the simulation, but it produces an accurate result. Stokes-Einstein is defined as (6) and for it to work every particle needs to be thought of as an isolated particle with that does not interact with other particles [4]. So, in the simulation particles can?t interact with each other.

$$D = \frac{k_B T}{6\pi\mu R_0} \tag{6}$$

In the equation k_B is the Boltzmann constant, T is the temperature of the liquid, μ is the dynamic viscosity of the fluid, and R_0 is the radius of the solute [4]. For water self-diffusion coefficient was used, because it is the rate of diffusion if it is no interacting with other molecules [7].

3   Simulation

The simulation followed the mixing of two types of particles mixing as a function of time.

3.1   Simulation for short

The simulation calculates the average displacement for both axis for every particle by integrating the effective velocity over time. The effective velocity depends on diffusion coefficient, time and a multiplier which is based on the bell curve. The multiplier also determines the direction of the movement. If the particle hits a wall then the simulation will stop working for that particles coordinate. Which is why there is a way to generate a dot that will not collide with the wall with the current parameters this way it is easier to interoperate the results. However the gaussian is much easier to notice from the line simulations. Then for every x y position a mean is taken from all the types of particles, then a heat map is generated using the data. This heat map shows the current positions of the particles, which can be used to track the diffusion.

3.2   Initial conditions

The simulations scale is mm/10 so, we can see actual changes in the fluid without making the time scale too big. The simulation used as an example was performed with a 20 mm/10 times 20 mm/10 open pipe with 10 particles/clumps of particles per x, y coordinate. There was no velocity applied

to the pipe and the integration was done in 0.2 sized steps.

The fluids used were water(l) as solvent and sucrose(aq) as the solute. It was chosen for no particular reason other than it is a sugar and therefore water-soluble. The simulation ignored all the interactive forces between these substances. Waters dynamic viscosity can be taken from the source $7.972 \cdot 10^{-4}$ [5], depending on its temperature 300 K. For water molecules the simulation uses the self-diffusion coefficient $2.299 \cdot 10^{-9}$ at the temperature 300 K from source [7].

Sucrose?s temperature was 350 K and Stokes radius in the simulation was chosen to be 5.4 Å based in the sources [6] findings.

3.3   Results

Using the Stokes-Einstein equation the diffusion coefficient for sucrose at temperature 310 K was $5.48 \cdot 10^{-10}$ m^2/s which is relatively close to the actual coefficient $6.97 \cdot 10^{-10}$ m^2/s[4], so we can presume that the sugar is a big enough molecule for the equation and that it can be used in the simulation. The diffusion simulation itself works quite well and produces a slide show of heat maps which show the evolution of the mixing as a function of time. The mixing process follows a bell curve where the sucrose concentration reduces spreads out, the peak of the concentration is found at the middle this can been clearly seen from figs 2-8.

As we can clearly see for figure 6-8 the probability for the particle to either direction is equal, so P(x,t) = P(-x,t) is true for the simulation. This is true for both axis as we can see from figure 3 and 4. Where the simulation produces a circle, with noticeable increase of concentration in the middle. So, the densities decrease as a function of time and the which cause the density bell curve to flatten as the time goes on. If we were to let the simulation run for a long time it would produce a uniform distribution like for example figure 9.

From the simulation we also notice that the diffusion has a notably higher

speed in the beginning where it takes only around 30 seconds to take over the first water row. For the second and third row it takes much more time to do this, from this we can determine that the particle speed depends on time, which is true. This can be especially noticed in the figures 3 to 4 where the times difference is 80 seconds, but it has just taken over one water row.
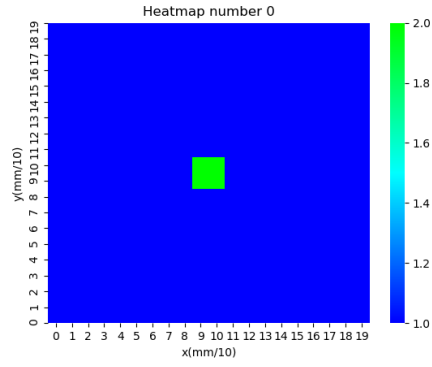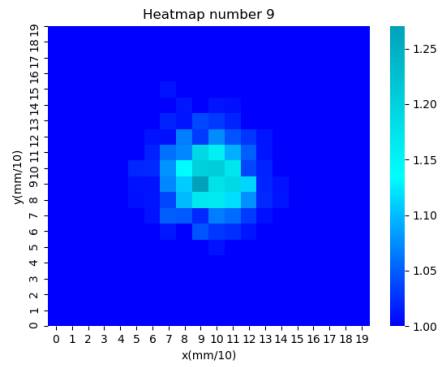

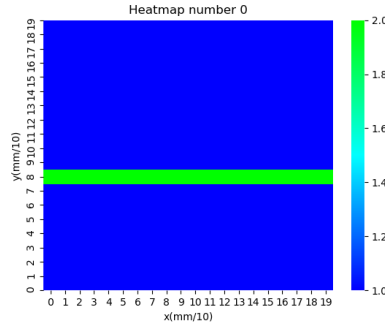Kuva 1: Dot simulation t= 0 s
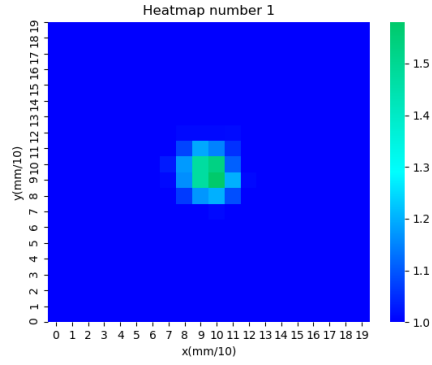
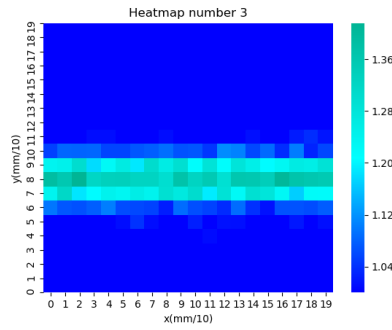Kuva 2: Dot simulation t= 20 s
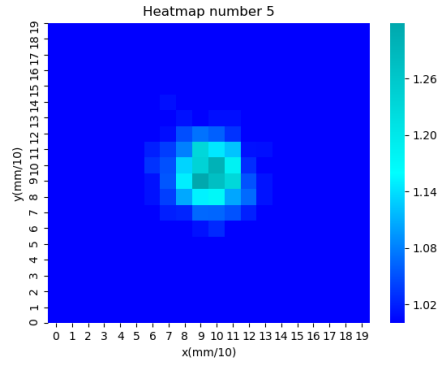
Kuva 3: Dot simulation t= 120 s
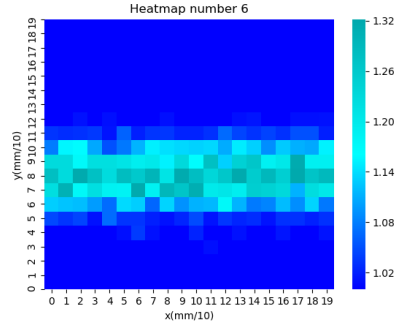

Kuva 4: Dot simulation t= 200 s

At the end of the simulation distribution of the sucrose particles do noticeably follow a sort of gaussian distribution. This means that there are more particles near the point where the sucrose was placed, because they haven´t wondered off yet and that the both ends have a similar concentration. This is easily seen in figures 5-8 where the uniform color has changed to a green blue with a green patch at the middle where the sucrose was originally placed and the ends look fairly similar. From figures 5 to 8 it is easy to notice the flattening of the bell curve and again if we were let the simulation to run at the end there would be an even distribution of particles (fig 9).
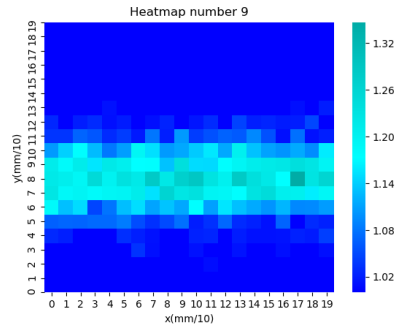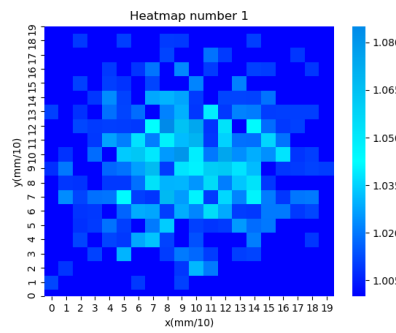

Kuva 5: line simulation t= 0 s

Kuva 6: line simulation t= 80 s

Kuva 7: line simulation t= 140 s

Kuva 8: line simulation t= 200 s

Kuva 9: Dot simulation t= 2000 s

Overall, I think the simulation performed well especially the line simulation shows the bell curve caused by the diffusion quite nicely. However the accuracy of the simulation is highly questionable and there were a lot of assumptions made. For example, the "integral"used and ignoring all of fluid dynamics. The code itself could be massively improved to make it run a lot faster (heatmap gen very slow) and there is most definitely a way to make the integration faster and much more accurate. But still the simulation produces good estimate of the result in a decent enough time.

Viitteet

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