FYS4460 -
Second compulsory project

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1 Parallellization

The most time consuming part of my program is in the function called findForces(). Here there is two four loops (one triple- and one quadruple- for loop), that runs through all the particles and calculates the forces. In parallellizing the code we seem to have to options; we can divide the system into cells (larger than the cells we already have), and calculate the forces in these cells in parallel (with the aid of MPI to communicate), or we can let the program run in serial except when we calculate the forces. I have chosen the latter option, where I use openMP to parallellize the loops. This is a much easier solution, because it just means adding a few lines of code in my original code. The back side to this solution is that it requires that we work on a shared memory computer, while the solution with MPI will run on a cluster. For now I am working on a shared memory computer, so it is fine, but if I want to run for a larger system I will consider using MPI.

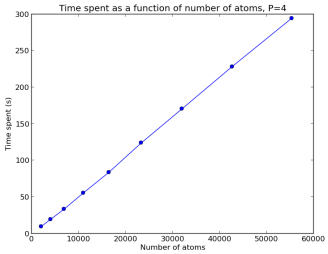
1.1 Efficiency

If it takes an amount of time, $T(N, P)$, to find the new state in a molecular dynamics code, the speed of the simulation may be characterized by

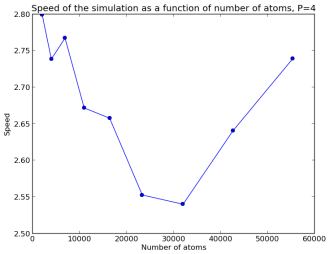
$$S_P = T(N, 1)/T(N, P)$$

where N is the number of atoms and P is the number of parallel processes.
The parallel efficiency of the method is

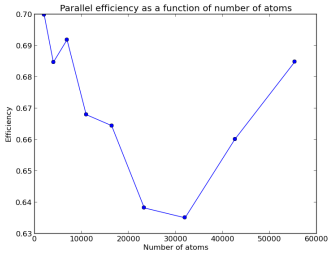
$$E_P = S_P/P. \tag{1}$$



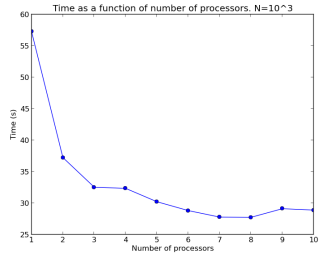
(a) Time spent with four parallel processes.



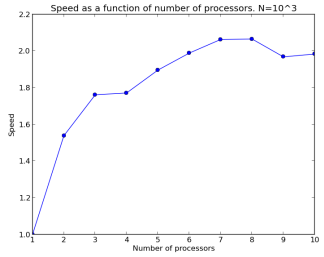
(b) The speed with four parallel processes



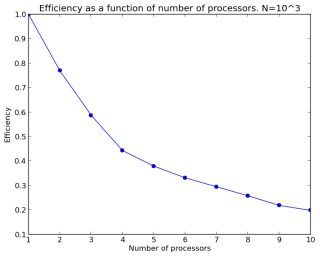
(c) The efficiency with four parallel processes



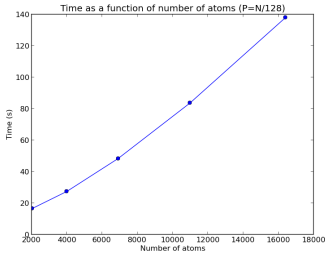
(d) Time spent with $N = 4 \cdot 10^3$, varying P.



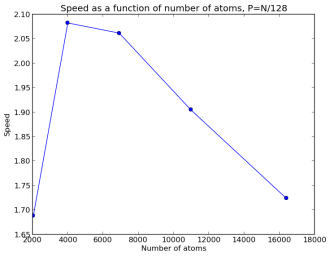
(e) Speed with $N = 4 \cdot 10^3$, vaying P.



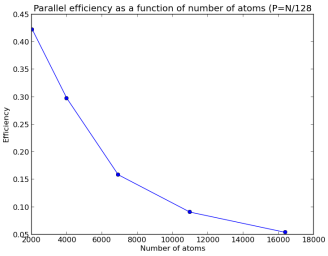
(f) Efficiency with $N = 4 \cdot 10^3$, varying P.



(g) Time spent for P=128N, varying both N and P.



(h) Speed for P=128N, varying both N and P.



(i) Efficiency for P=128N, varying both N and P.

Figure 1: Testing the parallellized program by varying P and N.

2 Generation of a porous matrix

Our plan to generate a porous material is to first generate a thermalized Lennard-Jones system, and then select a given part of the sytem to be the solid matrix. The simplest version is to freeze all the atoms in the matrix, meaning they are not allowed to move, but still let them interact with the particles that are allowed to move. One way to make pores is to generate randomly large spheres placed at random in the Lennard-Jones liquid, and choose to let the particles inside the spheres be frozen, or the other way around.

2.1 Cylindrical pore

To practice our pore-making-skills, the first task was to make a cylindrical pore with radius $R = 2nm$ at the center of a system with $N_x = N_y = N_z = 20$ unit cells of size $b = 5.72$A. First, the system is thermalized at $T = 0.851T_0 = 101.9K$. I made the matrix by letting the atoms know if they are able to move, or not. They all have an attribute called canMove, which is boolean true if the atom in fact is able to move. After thermalizing the system, I marked the particles outside the cylinder by setting “canMove“ to ”false“. Then, only the particles that are unable to move are written to a VMD-file (my program can also do it the other way around). In figure 2 we have a visualization of the matrix.

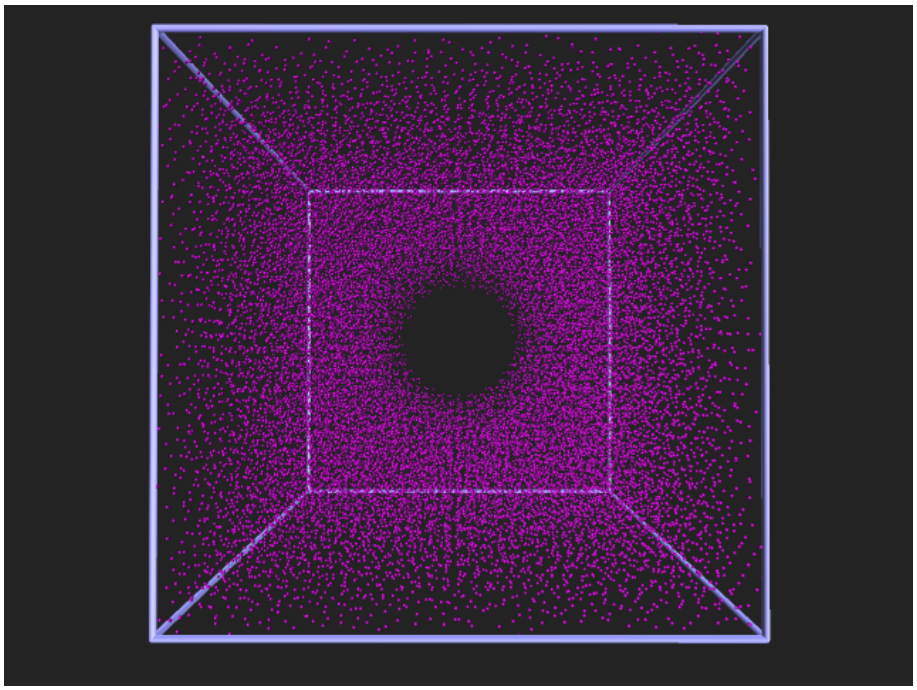


Figure 2: A cylindrical pore of radius $R = 2$ nm. The length of the system in each space direction is $20 \cdot 5.72\text{A} = 11.44\text{nm}$

2.2 First nano-porous system

In figure 3 you see the argon liquid with 20 pores at random positions. The blue particles are atoms that are not able to move. This is the state after having the thermostat on for 100 timesteps with temperature $T_{bath} = 1.05T0 = 125.7$, and then 200 timesteps without the thermostat on. The final temperature measured for this sytem was $124K$.

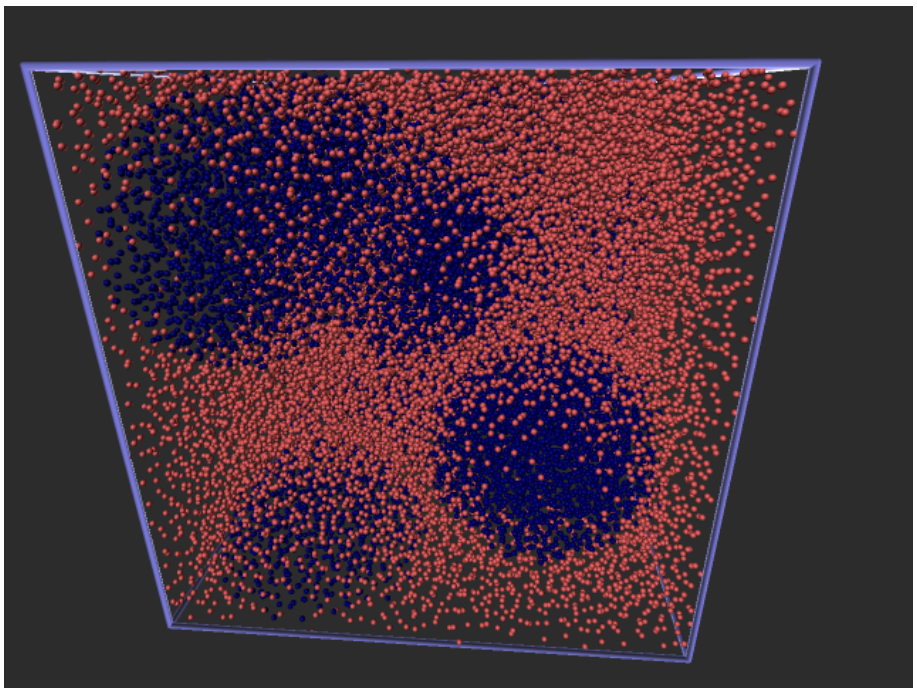


Figure 3: Argon liquid with 20 randomly sized and placed pores.

2.3 Porosity

The porosity, ϕ, is the relative amount of pore space in the volume. To calculate this I first found the average volume of each atom by dividing the total volume by the number of particles, before cutting out the pores. Then I just counted all the particles set as unmovable, and multiplied this number by the average volume to find the volume of the matrix.

$$V_a = V/N_{all}$$
$$V_{matrix} = V_a N_{matrix}$$

We can now set the porosity as

$$\phi = 1 - V_{matrix}/V \tag{2}$$

The porosity of the system visualized in figure 3 is $\phi = 0.500$.

3 Macroscopic measurements

We reduce the density of the fluid inside the pores (the movable particles) by randomly removing half the particles in the fluid from the system. Then we thermalize the system at $T = 1.5T_0 = 179.6$ K.

3.1 Evolution of temperature

I was interested in how the system would evolve if we didn't turn the thermostat on after reducing the density, so I ran an experiment for 1300 timesteps without thermostat. The evolution of temperature is shown in figure 4. We see that the system uses quite many timesteps before it reaches a temperature it is "comfortable" with, and this temperature is about 30 K colder than the maximum temperature it has in the beginning.
Figure 5 shows the evolution of kinetic and potential energy in the system without thermostat. Here we see that the total energy has the same value throughout the experiment, which is as expected.

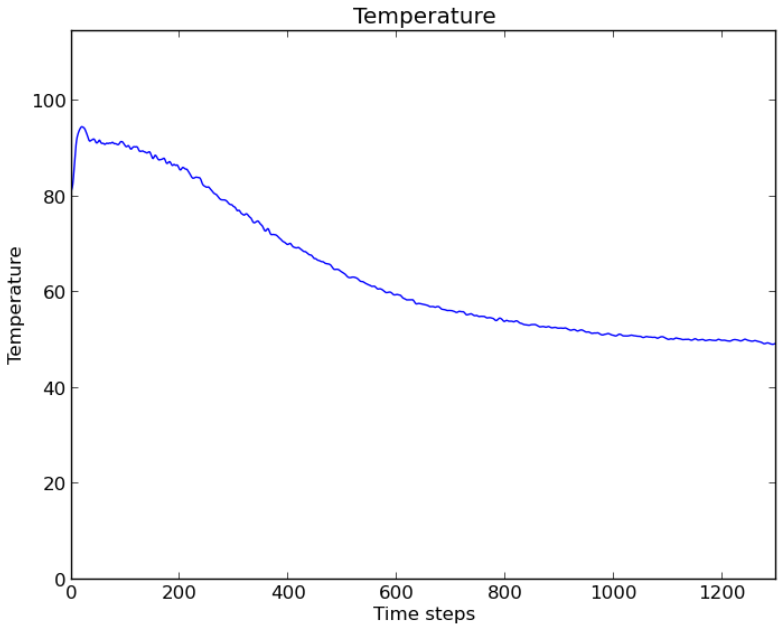


Figure 4: The evolution of temperature of the system after the reduction of fluid density.

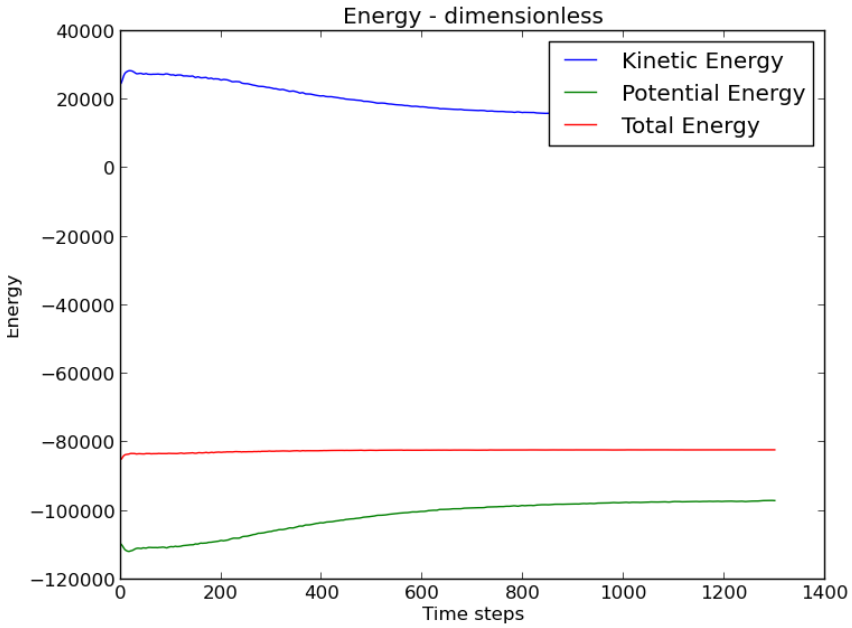


Figure 5: The evolution of energies for the system of pores after the fluid density is reduced.

Now, let's turn on the thermostat. Since the system used many timesteps to equilibriate without the thermostat, I decided to have the thermostat on for quite some time; the thermostat was on for 1000 time steps, and the last 300 time steps was without thermostat. The evolution of temperature is in figure 6.

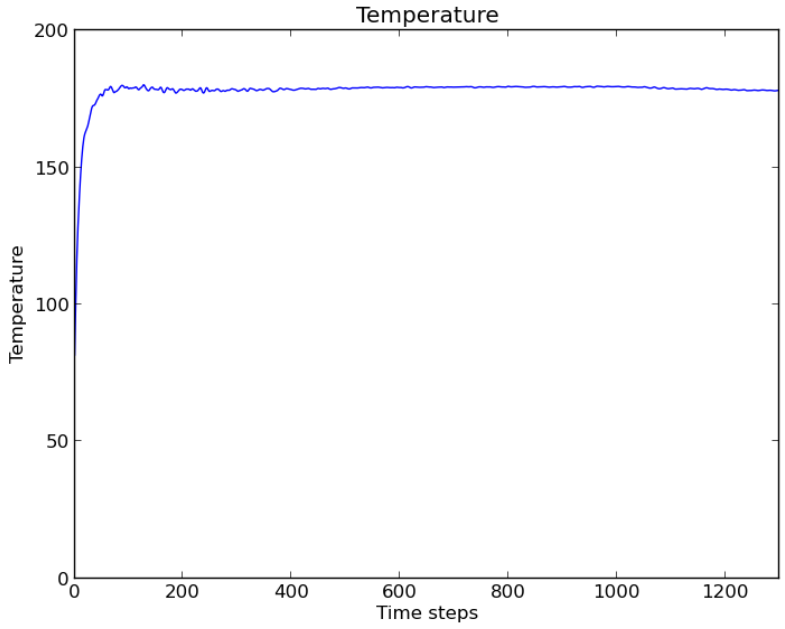


Figure 6: The evolution of temperature with thermostat on for the first 1000 timesteps, the last 300 without.

3.2 Spatial distribution of pressures

The system I did the spatial pressure analysis on is visualized in figure 7. In this picture the system is seen from below, to make it easier to compare with the pressure distribution seen in figure 8. The pressure distribution has large areas of zero pressure (blue in fig. 8), and surrounding these areas we what

looks like mountains of pressure contributions. It is not weird that we get the areas with zero pressure; this is due to the fact that my program does not calculate the forces between particles unable to move. Essentially, the forces between such particles are set to zero and therefore also the pressure. If we look at fig. 7 again, we see that areas with just blue particles have the same shape as the zero-pressure areas in fig. 8.

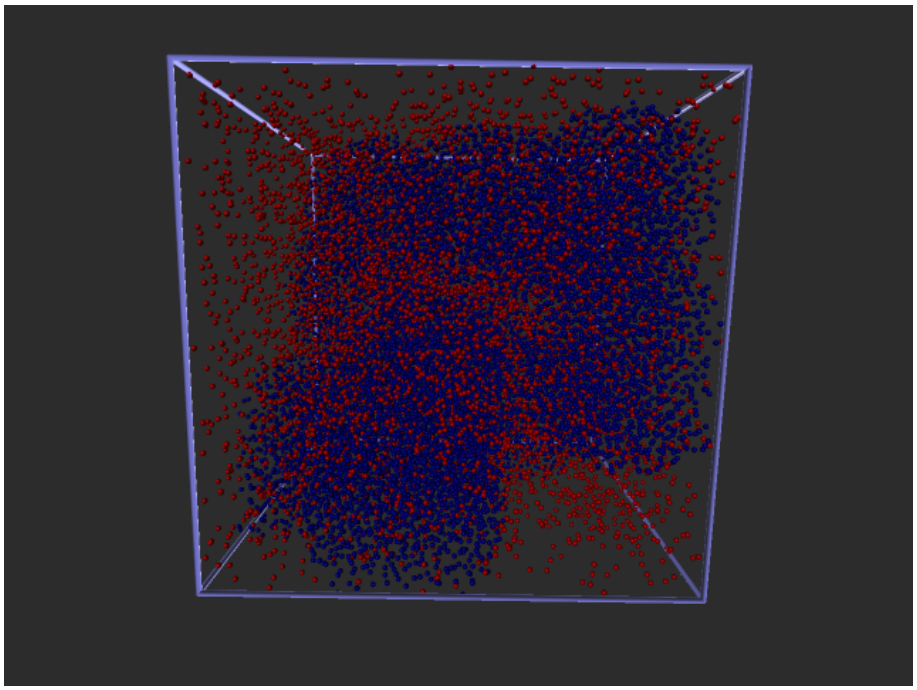


Figure 7: System with 20 pores seen from below. The blue particles are not able to move.

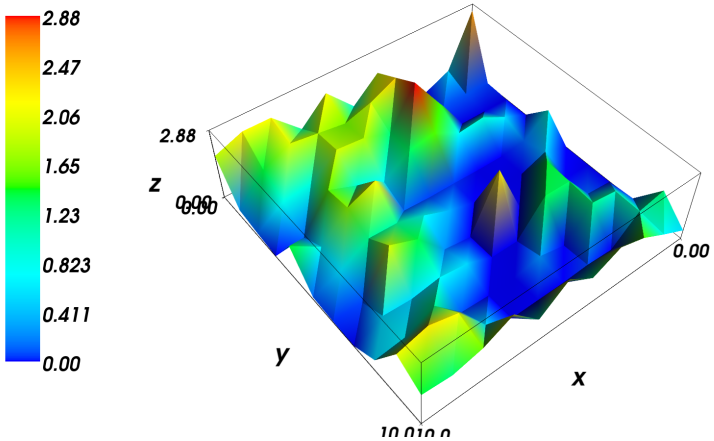


Figure 8: The spatial distribution of pressures in the system at T= . This is the layer of cells closes to $z = 0$.

3.3 Displacement

Starting from a thermalized porous system with low density fluid, I time evolved the system for 300 time steps. I measured the atomic displacement at every time step, and the result can be seen in figure 9. The porosity of this system is $\phi = 0.5$. As in project 1, we can find the diffusion constant, D, by the slope of the linear approximation to the displacement

$$\langle r^2(t) \rangle = 6Dt \tag{3}$$

With the linear approximation shown in green in fig. 9, we got the diffusion constant $D = 0.1179$.

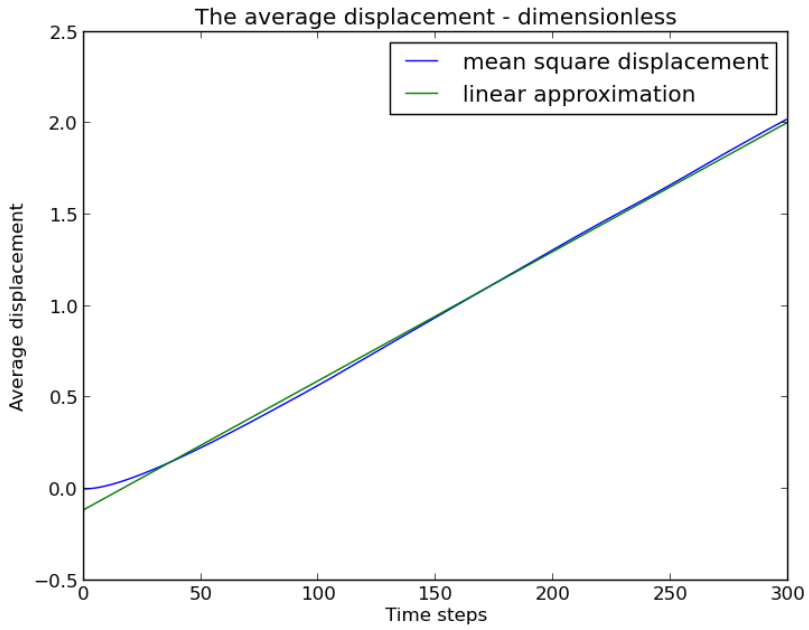


Figure 9: The displacement of atoms for a nano porous system with temperature at $T = 1.5T_0$.

4 Flow in a nano-porous material

The next, and last part of the project is to induce flow in the material by introducing an external force in the x-direction, $\mathbf{F} = F_x\mathbf{i}$. In the case of flow in a gravitational field, Darcy's law is usually formulated as:

$$U = \frac{k}{\mu}(\nabla P - \rho g) \tag{4}$$

where ρ is the mass density $\rho = \frac{Nm}{V}$. The last term in the parantheses can be rewritten:

$$\rho g = \frac{Nm}{V}g = \frac{N}{V}F_g = nF_g$$

where n is the number density $n = \frac{N}{V}$, and F_g is the gravitational force $F_g = mg$. We will not use mg as our force, but just insert a constant force in the direction of the cyllinder $\mathbf{F}$ as described above. In our system the pressure does not change much along the cyllinder, så $\nabla \approx 0$. Darcy's law for our external force

$$U = \frac{k}{\mu}nF_x \tag{5}$$

Now we will measure the flow profile $u(r)$ of a fluid flowing through a cylindrical pore due to a force along the cylinder. We will use $u(r)$ to estimate the fluid viscosity μ. When the system has reached a stationary state, we expect the flow profile to look like this:

$$u(r) = \frac{nF_x}{4\mu}(a^2 - r^2) \tag{6}$$

where a is the radius of the cylinder. To estimate μ we divide the radii into bins, and find $u(r)$ for each bin. Then, we calculate μ for each bin, and then estimate μ by finding the average.
The flow profile $u(r)$ is shown in figure 10. The number-density is shown in figure 11.

Figure 10: The flow profile of the fluid inside the cylinder.

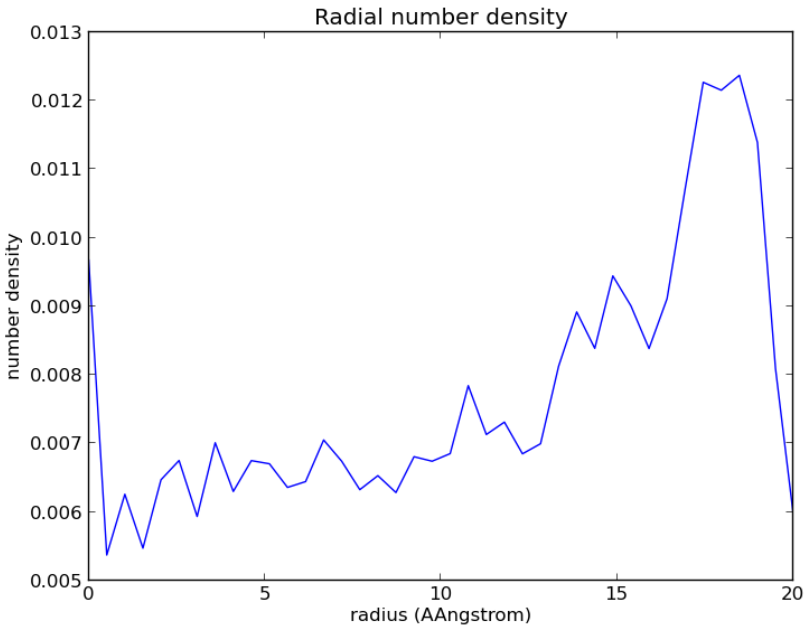


Figure 11: The number density as a function of radius in the cylinder with a force Fx=1.

The curves in figure 11 and 10 looks quite good, but we see that the maximal point of the "parabola" in fig. 10 is not at $r = 0$ which is not so good, and the slope on the right side of the plot is not steep enough. Other than that, they look okay, but I had trouble repeating the success, so I don't know how trust worthy they are. I had trouble reaching a stationary state; it seemed the temperature would not stop increasing. Based on experiments with between 2000 and 10000 time steps prior to the measurements, I got a viscosity around 60 in md-units. This corresponds to $\mu = 0.005\text{kg}/(\text{sm})$.
Now that we have found the viscosity for a given fluid, we can let the same fluid flow through different

nano porous materials and use Darcy's law (eq. 5) to find the permeability, k, for the different materials:

$$k = \frac{U\mu}{nF_x}.$$

All we have to do now is to measure U, which is a volume flux through an area in the media. I find this by counting the number (S) of particles moving through one of the walls in my cubic system (chose the xy-plane where z=0). If the particle moves with velocity in the positive z-direction I add 1 to the total sum (S+=1), but if it moves in the opposite direction I subtract 1 from the total sum (S-=1). The volume flux is then

$$U = \frac{SV_a}{t}$$

where V_a is the volume of each atom and t is the time running the measurement of S. Since I am running out of time I only find the permeability for two systems with different porosity.
For a system with porosity $\phi = 0.5$, I obtained a permeability $k = 0.0066\mu m^2$.
For a system with porosity $\phi = 0.2$, I obtained a permeability $k = 0.00122\mu m^2$.
It appears that the permeability decreases as the porosity decreases, which is quite intuitive.