Project 2, Fys4460

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(c) An Argon system of $N_x = N_y = N_z = 20$ unit cells was prepared. The system was initialized with a temperature of 300 K before a thermostat thermalized it at 102 K.

(d) A cylindrical pore of radius $R = 20$ Å was cut out in the middle of the thermalized system. Each atom was given the property "moving" or "not-moving", based on its position. The atoms inside the cylinder could move, the atoms outside the cylinder could not move.

(e) After a new system had been thermalized, 20 spheres were cut out of the system. The spheres were given a random position and a radius between 20 and 30 Å. The positions of all the atoms were investigated to find out if they were inside one of the spheres. The atoms inside the spheres were given the property "not-moving", and the atoms outside were given the property "moving".

The theoretical porosity of a system with 20 non-overlapping spheres was found by calculating the volumes of the random spheres, subtracting it from the total volume of the system, and dividing this on the total volume of the system. This ratio was found to be 0.05.

An estimate of the actual porosity of the system was found by counting the number of atoms that were allowed to move, and dividing this on the total number of atoms in the system. This ratio was found to be 0.40. In the real system the spheres overlapped, which made it possible for more atoms to move, than if they had not been allowed to overlap.

(f) After thermalizing the system at 102 K before cutting out the spheres, the system was thermalized again at 126 K. The ouput was visualized in VMD.

(g) After the spheres had been cut out of the system, a random number between zero and one was generated for each atom with the ability to move. If the number was below 0.5, the atom was given the property "removed". The default property for all the atoms was "not-removed". This gave the system approximately half the original density. The forces were only calculated for atoms that could move, and while the non-moving atoms contributed to the forces, the removed atoms did not contribute.

After half the atoms had been removed, the system was thermalized again at 180 K. The temperature was measured after the density was decreased. The plot can be seen in figure 1. The temperature increases as the thermostat is turned on after the first few time steps and appears to stabilize after the thermostat is turned off. The equation that was used was

$$T = \frac{2}{3Nk_B}\langle E_k \rangle$$

The equation that was used to calculate the pressure of the system was

$$P = \rho k_B T + \frac{1}{3V}\sum_{i<j} \vec{F}_{ij} \cdot \vec{r}_{ij}$$

The spatial distribution of the pressure can be seen in figure 2 and 3. The first shows the pressure distribution in the xy-plane for $z = 0$, the second plot shows the pressure for the plane when $z = L/2$. The pressure was calculated for each

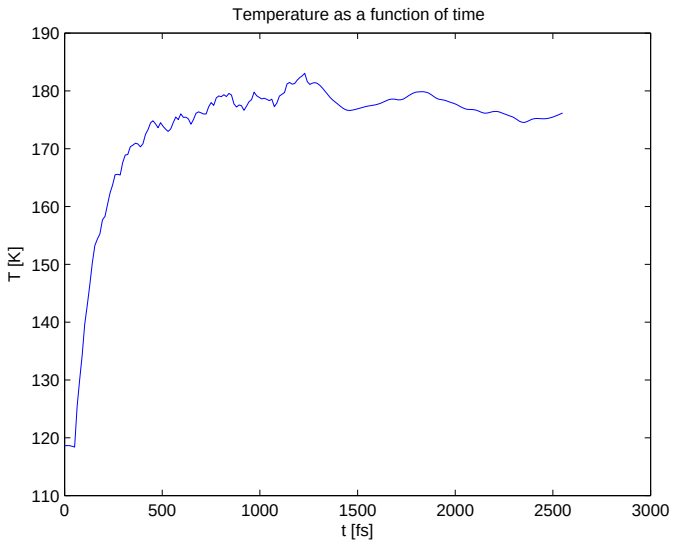

Figure 1: Temperature plotted against time for the fluid in the nano-porous system. The measurement begins after the density has been diminished. The thermostat is turned off after the desired temperature has been reached.

cell in the system, which consisted of $11 \times 11 \times 11$ cells. When calculating the pressure, the interactions between moving and non-moving atoms were taken into account, but not interactions between non-moving atoms. If there were no moving atoms present, the temperature of the cell was set to zero. It is possible that the negative pressures are a result of few atoms in the cell, possibly as a result of the cell containing both moving and not-moving atoms. The pressure equal to zero probably means that the cell was inside one of the solid spheres.

(h) The mean square displacement $\langle r^2(t) \rangle$ for the fluid in the nanoporous system is plotted in figure 4. The equation that was used was

$$\langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^{N} (\vec{r}(t) - \vec{r}_{initial})^2$$

The increasing values of the displacement suggests that the fluid is diffusing through the system, as opposed to oscillating around a fixed point.

(i) Darcy's law describing flow can be written like this

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

when the flow is in a gravitational field. k is the permeability and μ is the viscosity. If the external force is $\vec{F} = F_x \hat{i}$, the term ρg can be replaced.

The density ρ can be written $\rho = Nm/V$, the density of atoms can be written

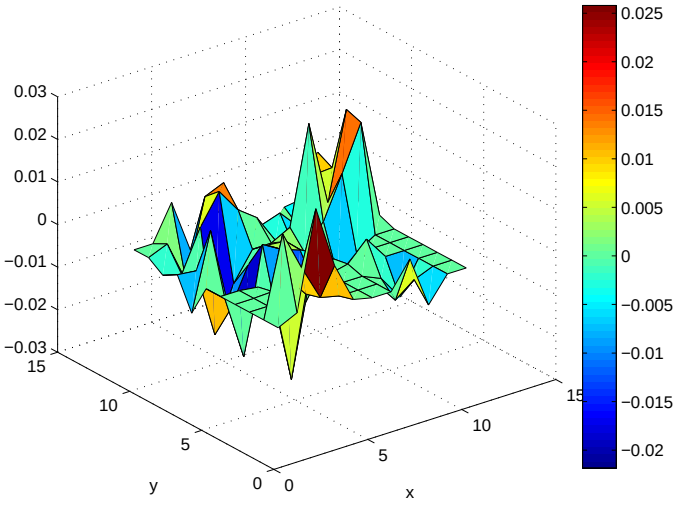

Figure 2: Spatial distribution of pressure in the x- and y-directions for z-cell number 0. The pressure was averaged over 100 time steps. The units are eV/Å^3.

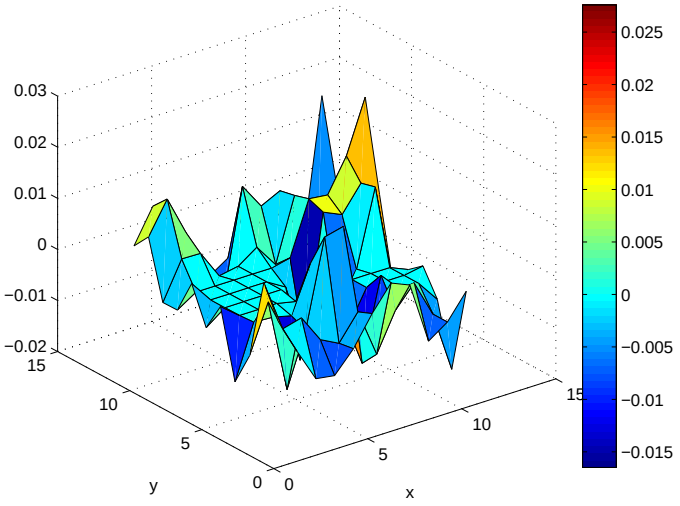

Figure 3: Spatial distribution of pressure in the x- and y-directions for z-cell number 4. The pressure was averaged over 100 time steps. The units are eV/Å^3.

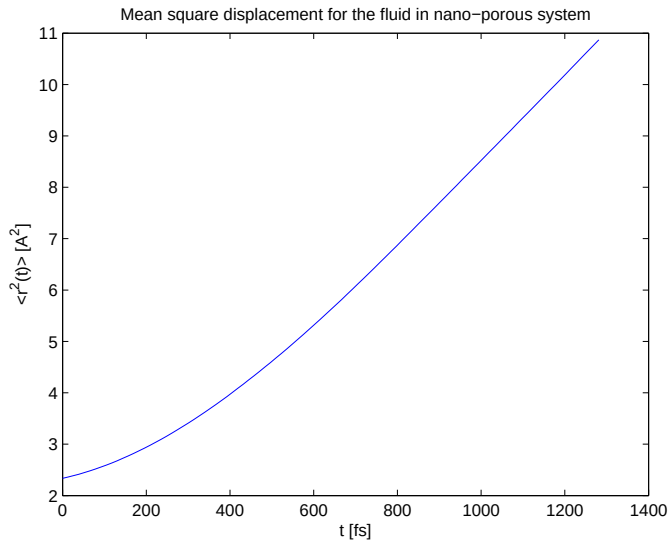

Figure 4: Mean square displacement as a function of time.

$n = N/V$ and the force can be written $F_x = ma = mg$. This gives

$$\rho g = \frac{Nm}{V} g = \frac{N}{V} mg = nF_x$$

This term can replace ρg.

(j) If a fluid flows through a cylindrical pore, the forces acting on it are caused by the pressure differences in the ends of the cylinder, and the stress caused by the differences in velocity. This gives the equation

$$\mu \frac{\partial}{\partial r}(r \frac{\partial u}{\partial r}) + r \frac{\partial P}{\partial x} = 0$$

Assuming that $\partial P/\partial x$ can be approximated by $\Delta P/L$, this equation has the solution

$$u(r) = \frac{\Delta P}{L} \frac{1}{4\mu}(a^2 - r^2)$$

for the velocity of the fluid in the cylinder, where μ is the viscosity and a is the radius of the cylinder.

Since the flow in this project is not being driven by a difference in pressure, but an applied force F_x on each particle per volume, we can set up the equation:

$$\mu \frac{\partial}{\partial r}(r \frac{\partial u}{\partial r}) + rnF_x = 0$$

which has the solution:

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

This equation can be used to estimate the fluid viscosity.

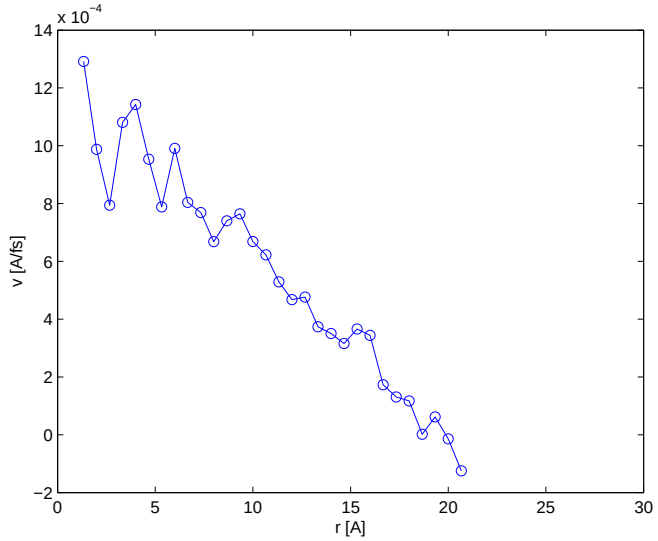

Figure 5: Flow profile $u(r)$ for the velocities in the direction of the cylinder. The results were averaged over all particles and 1000 time steps.

The external force was applied for approximately 20000 time steps with $\Delta t = 0.006$ in dimensionless units. A thermostat was used in the beginning of the simulation. The measurements were averaged over the last 1000 time steps. The temperature of the fluid gradually increased during the whole simulation.

The visualization of the results showed a lot of movement from the particles in the cylinder, but it was difficult to see a flow. However, the measured results show that there was a small flow in the system.

Figure 5 shows the flow profile $u(r)$ for a fluid in a cylindrical pore due to the force $F = 0.1\epsilon/\sigma$. $u(r)$ was found by finding the average velocity in the direction of the cylinder for all the particles in the cylinder. The shape of the curve is as expected from the theoretical equation. The velocity is largest in the middle of the cylinder ($r = 0$) and goes to zero as the radius goes toward a. It is possible that the curve could have been smoother with a larger interval to measure over.

In figure 6, the number density of the particles is plotted as a function of the radius. It appears to be almost the same along the whole cylinder, but it increases at the edges.

The viscosity μ of the fluid was found using the previous equation

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

Using the measured values for $u(r)$ and $n(r)$, the average value for the viscosity was found to be approximately 0.5 ev·fs/Å^3. This number was found using results from simulations different cylinder radius.

(k) In order to find the permeability k, one can use Darcy's law. Using the

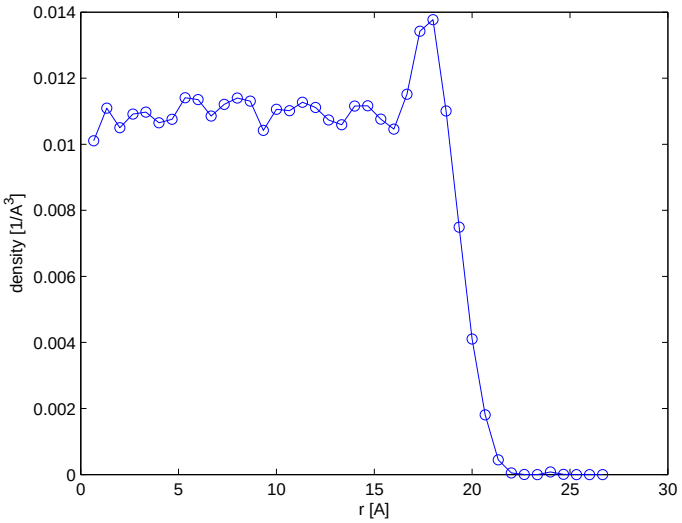

Figure 6: Density profile for the particles in the cylinder. The results were averaged over all particles and 1000 time steps.

force F_x instead of the pressure gradient gives the equation:

$$U = \frac{k}{\mu} n F_x$$

This gives the equation:

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

The force was given, the density and the flow U were measured, and the viscosity was calculated. U was found by counting the number of particles that passed through a cross-section of the cylinder for each time step and dividing by the time step and the cross-sectional area.

The theoretical estimation of the permeability as a function of porosity for cylindrical pores, is

$$k = \frac{\Phi a^2}{8}$$

The porosity Φ is given by

$$\Phi = \frac{V_{pores}}{V}$$

By changing the size of the cylinder in the simulation, the permeabilities k in figure 7 were found. The theoretical estimation is also plotted. One of the porosities was simulated twice, using 10000 and 20000 time steps. The other simulations all used 20000 time steps.

The permeabilities calculated from the simulations appear to show a good match for the smaller cylinders, but as the cylinders increase in size, the theoretical estimates increase faster than the measured results.

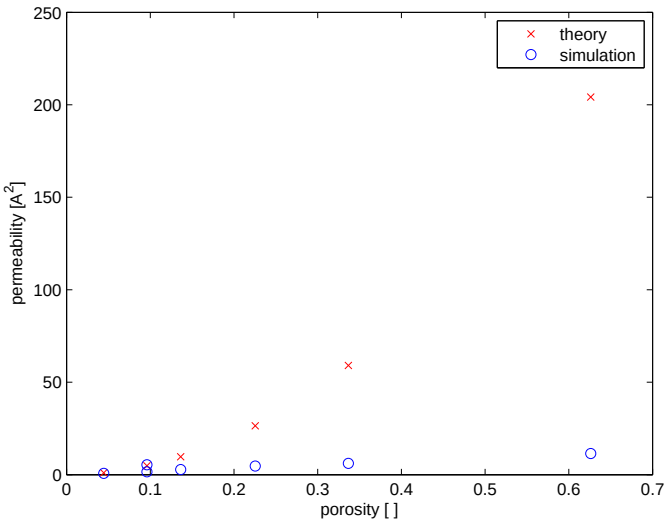

Figure 7: Permeability as a function of porosity.