

FYS4460

PROJECT 2:

ADVANCED MOLECULAR DYNAMICS

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1. GENERATING NANO-POROUS MATERIAL

We prepare a liquid Argon system of size $N_x = N_y = N_z = 20$ unit cells, each with side length $b = 5.72\text{\AA}$. To use this length in a face centered cubic lattice in our simulation, we must calculate the reduced density,

$$(1) \quad \rho^* = \frac{n\sigma^3}{b^3},$$

where n is the number of atoms in a cell, 4 in the case of a fcc lattice. We then thermalize the system at $T = 0.851$ (lj-units), using the Nosè-Hoover thermostat. Once thermalized, we cut out a cylindrical pore of radius $r = 20\text{\AA}$ in the $y - z$ plane from $x = 0$ to L , and "freeze" the atoms outside of the cylinder by setting their velocity to zero and keeping them fixed in place. The atoms inside the cylinder are free to move as before, but are not constrained by the frozen atoms, still including their interactions.

We can also make a different type of porous structure, by randomly packing a number of spheres of a given size, and mark the atoms within these spheres as non-moving. In figure 1.1, we have packed 20 spheres in uniformly random locations, each with random radii of $r \in [20, 30]\text{\AA}$. The porosity of the system is defined as the ratio of the porous and total volume,

$$(2) \quad \phi = \frac{V_{space}}{V_{total}}.$$

In this system, we approximate this by counting the number of mobile atoms and the number of total atoms, which gives a porosity of $\phi = 0.45$. Since we allow our spheres to overlap, it makes sense that the porosity of this system is higher than what we would expect in a system of non-overlapping spheres. We might, however, end up with spheres which are suspended in space without contact with any other solid material, which is not exactly very realistic.

We now wish to study a lower density system at $T = 1.5$. After thermalizing the system and the spheres have been defined, we randomly delete 50% of the flowing atoms, effectively reducing the density by one half. Figure 1.2 shows the temperature of the flowing atoms as a function of time. In an attempt to visualize the spatial distribution of the pressure, we calculate the stress on each atom within a cross section of the material divided into bins, and plotted the magnitude of this quantity. This is shown in figure 1.3. As the pressure is defined as stress per atom volume, the units of pressure is a bit unclear, but the main idea still comes across.

The mean squared displacement of this system is shown in figure 1.4, which is linear for $t > 0$, as expected. By using the Einstein relation, we find the diffusion constant to be

$$(3) \quad D = \frac{\langle r^2(t) \rangle}{6t} = 0.014 \frac{\sigma^2}{\tau}$$

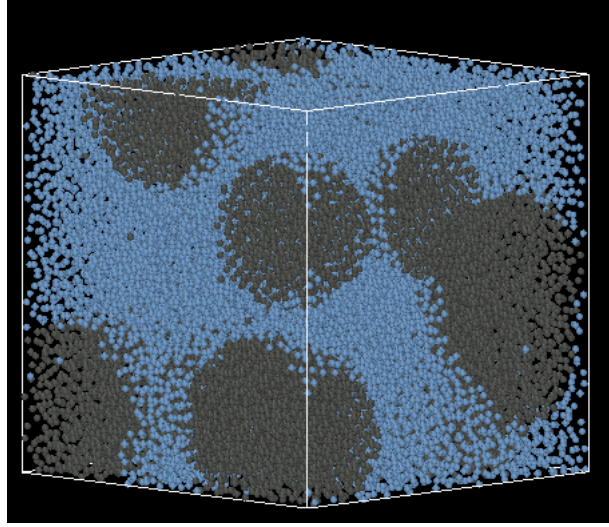


FIGURE 1.1. Randomly placed frozen spheres with radius $r \in [2, 3]$ nm in a porous structure. Porosity of the system is $\phi = 0.45$.

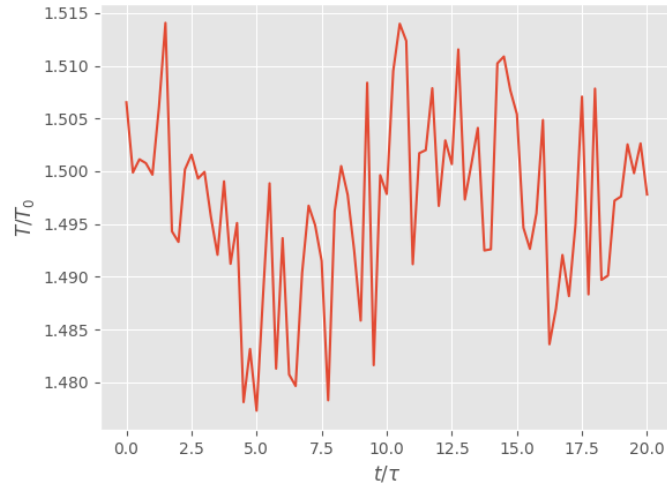


FIGURE 1.2. The time evolution of temperature of the porous system of spheres.

2. FLOW IN A NANO-POROUS MATERIAL

Darcy's law states that the volume flux density of the flow of a fluid with viscosity μ through a porous material with permeability k is

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

where ∇P is the external pressure gradient, ρ is the mass density and g the acceleration due to external forces. By Newton's 2nd law, we have that the net force in the x -direction on all the

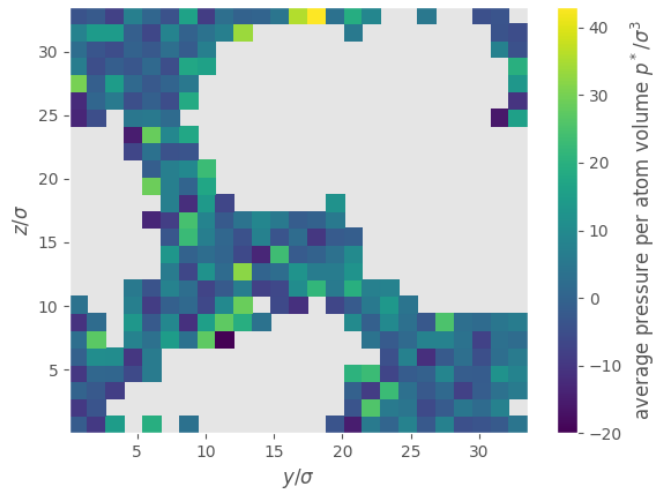


FIGURE 1.3. Cross section of the porous structure, showing the spatial pressure distribution of the system at $T = 1.5$. White areas represent the matrix of spheres.

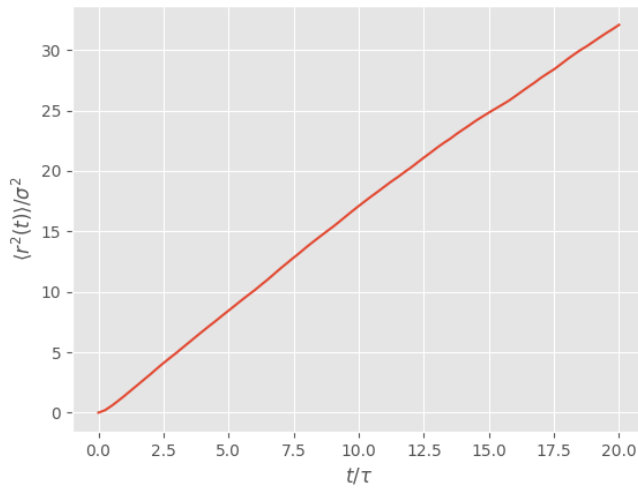


FIGURE 1.4. Mean squared displacement of the nano porous system.

particles is

$$(5) \quad NF_x = Nmg.$$

Dividing this by the volume, we have that

$$(6) \quad \frac{N}{V}F_x = \frac{Nm}{V}g,$$

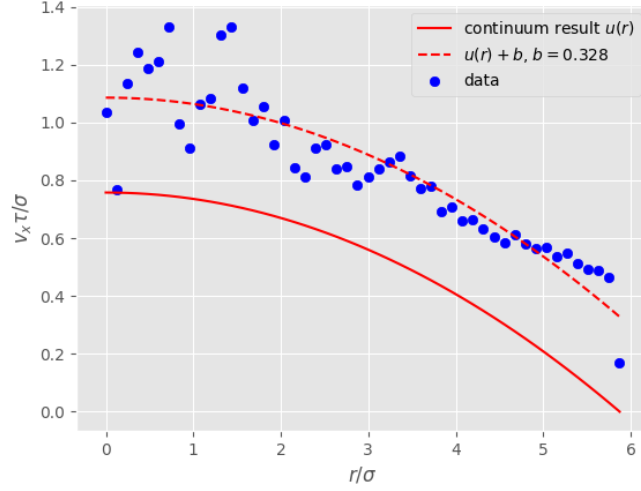


FIGURE 2.1. Average radial velocity in the x -direction of liquid argon flowing in a cylinder of radius $a = 2$ nm.

which gives us

$$(7) \quad nF_x = \rho g,$$

where $n = N/V$ is the number density of the system. Inserting this into 4 yields

$$(8) \quad U = \frac{k}{\mu}(\nabla P - nF_x).$$

One can also show that the velocity profile of a laminar flow of fluid through a pipe of radius a with an externally applied force nF_x is given by

$$(9) \quad u(r) = \frac{nF_x}{4\mu}(a^2 - r^2).$$

Using this equation, we can determine the viscosity of the fluid by measuring $u(r)$ in our simulations, and simply fitting μ to this data. We have chosen to simulate liquid argon of the same density as done in the sphere material above ($n = 2/b^3$), in a system with a single cylindrical pore of radius $a = 2$ nm, adding a force in the x -direction of $F = 0.1 \epsilon/\sigma$. This is done by thermalizing the full system at $T = 0.851$, before cutting out the cylinder and deleting half of the flowing atoms. We also add the force to each flowing particle at this stage, and since equation 9 is only valid for fluids in a stationary state, we let it run for (a rather arbitrarily chosen) 10000 time steps. At this point we begin recording data, for an additional 5000 steps. The velocity profile of the fluid is done by sorting the x -component of the individual atom velocities into bins and averaging over the recorded data. We find that the viscosity is $\mu = 0.48 \tau \epsilon/\sigma^3$, and the comparison of the data with the continuum results are shown in figure 2.1. This value for the viscosity is about three times lower than any reference point I could find elsewhere. Some of the reasons for this may be that we had some issues in the simulation. One being that the velocity at $r = a$ was not zero, which is what we would expect from such an experiment, but it is also an important assumption in deriving equation 9. Another important point is that we did not use a thermostat in the final 5000 time steps, and the temperature rose from $T = 0.84$ to $T = 0.97$, which is quite a bit higher than for liquid argon. It seems reasonable that both of these factors

would contribute to yielding a higher viscosity of the fluid, as the total flow is obviously higher when it is non zero at the edges, and one would also think that an element in its gaseous form would flow more freely than it's liquid counterpart.

Having found the viscosity of the fluid, we can now attempt to categorize a porous material in terms of its permeability k . We measure the permeability as a function of porosity by generating a range of materials with different porosities, and measure the center of mass flow rate of the argon in each simulation. Using equation 8 we have that

$$(10) \quad k(\phi) = \frac{U(\phi)\mu}{nF_x}.$$

. Here we have chosen to create materials with 27 evenly spaced spheres, as depicted in figure 2.2,

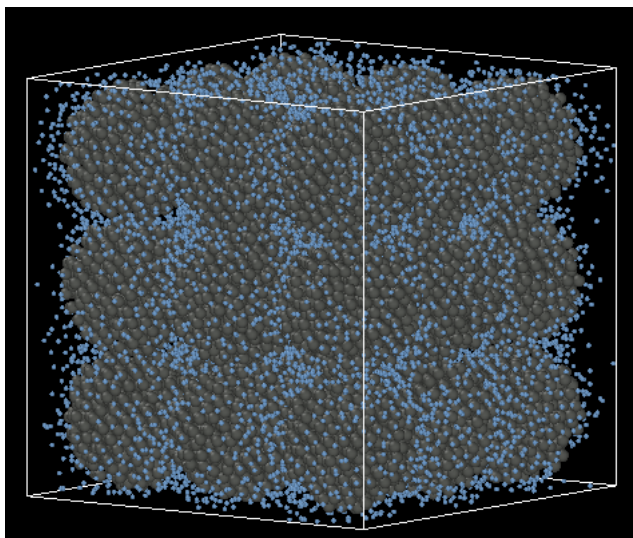


FIGURE 2.2. Porous material consisting of 27 evenly spaced spheres.

and increase the radii of the spheres in each new simulation. We also let the system equilibrate for 14000 time steps before collecting data. It can be shown that a material consisting of periodic spheres has a permeability given by

$$(11) \quad k = \frac{2a^2}{9C_D(1-\phi)},$$

where a is the radius of the spheres and C_D the drag coefficient. Comparing this to the Carman-Kozeny expression for random packing of spheres,

$$(12) \quad k = \frac{a^2}{45} \frac{\phi^3}{(1-\phi)^2},$$

we see that the drag coefficient is $C_D = 10(1-\phi)/\phi^3$. In figure 2.3 we show the results from the simulations, and compare it to the theoretical model in equation 12. The figure shows our simulated results are relatively close to the theoretical model for porosities in the range $\phi \in [0.5, 0.8]$, but in the case where there is hardly any material blocking the flow, the measured permeability looks to slow down. One likely explanation for this behaviour may be that we have not let the system equilibrate enough to reach a stationary state, which would mean that the measured velocity of the system is lower than its full "potential".

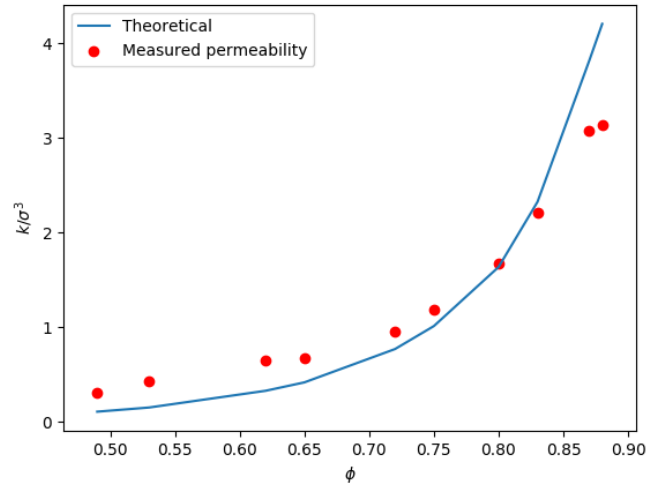


FIGURE 2.3. Measured permeability from simulations of flowing argon in a media of regularly packed spheres, compared with the theoretical model of random packing of spheres.