FYS4460 Project 2:
Advanced Molecular Dynamics Modeling

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Abstract

In this article we look at generating nano-porous materials using LAMMPS.

Contents

1 Introduction

In this project we will develop a molecular dynamics code to model the behavior of nano-porous materials. Further, we will apply this model to measure and discuss diffusion, flow through and deformation of the material. We study the effects using the Lennard-Jones potential, however there will be room to expand the code into more advanced potentials.

2 Theory

2.1 Nano-porous Materials

Nano-porous materials consist of a regular organic or inorganic framework supporting a regular, porous structure. The nano prefix signifies that the pores are in the nano scale $L \in [1\text{nm}, 100\text{nm}]$. The un-moving, or relatively un-moving, part of the nano-porous material is often referred to as the skeleton, the matrix or the frame of the material.

2.2 Generating a Nano-porous Material

In order to study a nano-porous material we follow three steps: First we generate the nano-porous matrix, second we fill the matrix with the particular fluid we wish to study, and finally we study the physical processes and properties of the system we are interested in.

2.3 Studying Flow in Nano Tubes

In order to study flow in nano tubes and pipes there are several approaches.

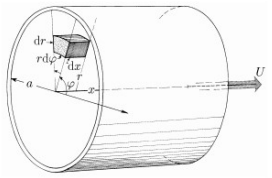

Figure 1: Diagram of a tube element where we have laid the x-axis along the motion of the fluid through the pipe. One fluid element is described by the size $d\varphi dr dx$, the tube radius is a and the flow velocity is U. The image is from [2], on page 50.

One might imagine setting up a pressure differential, over the x-axis, as a boundary condition in the code to obtain a flow, another approach might be to connect the tube to two reservoirs with different particle densities. In this article we will opt for modelling the flow in our nano tube in much the same way as we model flow due to the force of gravity.

2.4 Flow Profile in Tubular Flow

2.5 Darcy's Law of Flow

Darcy's law was initially determined experimentally by Henry Darcy [3] who was working on the flow through beds of sand for use in oil extraction.

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

Darcy's law was discovered experimentally, but has been shown to be derivable from the Navier-Stokes equation. It can be seen as an analogue to Omh's law in electricity and Fourier's law in heat transport, the relation is described in the appendix (A). For our implementation of Darcy's law we wish to rewrite it in terms of a driving force along the x-axis, we start by considering the force on a single particle i

$$\begin{aligned} \mathbf{F}_{x,i} &= m_i \mathbf{a}_{x,i} \\ \sum_i^N \mathbf{F}_{x,i} &= \sum_i^N m_i \mathbf{a}_{x,i} \\ N\mathbf{F}_x &= Nm\mathbf{a} \\ \frac{N}{V}\mathbf{F}_x = \frac{Nm}{V}\mathbf{a}_x &\rightarrow n\mathbf{F}_x = \rho \mathbf{a} \end{aligned}$$

Thus, we can rewrite Darcy's law for a horizontal driving force as

$$\mathbf{U} = -\frac{k}{\mu}(\nabla p - n\mathbf{F}_x)$$

which is easily implemented in a LAMMPS script in order to study flow in nano-porous materials.

3 Method

3.1 Generating a Nano-porous Material

This section will be a sort of "Hello World!" for advanced molecular dynamics. Following is a description, in addition to code excerpts, of how the nano-porous material consisting of Argon was generated and visualized using LAMMPS and OVITO. In order to prepare a regular Argon system without any structure, i.e. just a box filled with particles, we follow the same procedure as done in Project 1 ([1], [4]). This time $N_x = N_y = N_z = 20$ unit cells were used, each of size $b = 5.72$Å, resulting in a 11.44nm simulation region, and the system was thermalized at $T = 0.851$. Subsequently, a cylindrical pore of radius $R_c = 2nm$ was '*cut out*' along the x-axis using the following LAMMPS markdown

Cylinder Region

```
variable radius equal 20/${b}
variable center_y equal ly/2
variable center_z equal lz/2
region cylinder cylinder x ${center_y} ${center_z}
${radius} EDGE EDGE units box
group cylinder_group region cylinder
set group cylinder_group type 2
group frozen subtract all cylinder_group
velocity frozen set 0 0 0
unfix 1
fix 1 cylinder_group nve
```

Reading line by line here the first four lines we define various sizes defined which are defined in the task and needed to place the cylinder in the desired location, along the x-axis in the middle of the box.

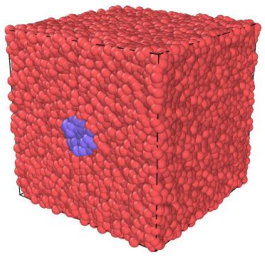

Figure 2: Cylinder cut out without modification of the frozen atoms. Ambient occlusion is turned on simply because I liked the look of it.

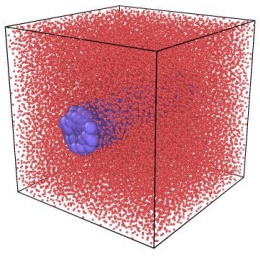

Figure 3: Cylinder cut out where the frozen atoms' radii are modified to be 0.2 of their '*actual*' size. This was done to show that the cylinder indeed goes through the whole simulation box. Important to stress that the dynamics of these two visualizations are exactly the same, this size modification was just added in post-processing.

The next three lines specify the atoms in the cylinder region as their own group in LAMMPS and we create a new group called frozen which is defined as the group of all atoms with the atoms in the cylinder group subtracted. The next two lines specify that we do not want to let any of the atoms in the frozen group to move, this is done by explicitly setting their velocities to zero and unfixing them. The last line tells us we wish to run a nve simulation on the atoms in the cylinder group. In this code nothing really happens when it is ran, except for self-diffusion, as there is no force being applied to the atoms in the cylinder group. This is the next step we wish to implement. However, it turns out that LAMMPS already has a function which does exactly what was discussed in (2.5), i.e. lets one add a force in a specified direction to a specified group: *fix force cylinder_group addforce 0.1 0.0 0.0* in our case.

3.2 Randomized Nano-porous Materials

Next we tackle generation of randomized configurations of nano-porous materials. To do this we only need to implement some very basic randomization and a single loop in LAMMPS. Following is the necessary code to generate a collection of nano-pores and to group them in order to integrate them later.

Generating Pores in LAMMPS

```
variable radius_min equal 20/${b}
variable radius_max equal 30/${b}
variable a loop 20
label pore_loop
variable x_1 equal random(0, ${lx}, ${seed})
variable y_1 equal random(0, ${ly}, ${seed})
variable z_1 equal random(0, ${lz}, ${seed})
variable radius_1 equal random(${radius_min},
${radius_max}, ${seed})
region $a sphere ${x_1} ${y_1} ${z_1}
${radius_1} units box
next a
jump random_argon.md pore_loop
```

Here the first two lines set up our minimum and maximum pore radii, and the next line defines our loop. The three following lines together choose a unique random location to center our pore at within the simulation box. The next two lines define a random radius in the range sat by the first two lines of the script and defines a spherical region based on this radius. The last two lines are just the syntax for loops in LAMMPS. Calculating the porosity of a material generated in this way using LAMMPS is pretty simple, we just count the atoms in the pore_group and divide this by the count of all the atoms; *variable porosity equal count(pore_group)/count(all)* and we save this number.

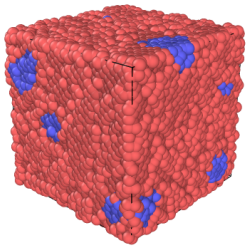

Figure 4: Result of the script described above.

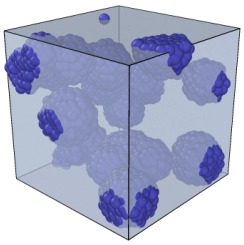

Figure 5: Exact same result as the previous figure except the size of the frozen group is set to 0.01 and a 30%transparent surface mesh was generated on the frozen group. Here we see the internal structure of the generated nano-porous material. This specific material has porosity $\phi = 0.16246875$

3.3 Studying a System with Half Density in Pores

in order to study systems with different densities in the pores we simply remove the desired percentage from each pore when we generate it in the pore loop. Not much else is different from the previous script. We calculate the mean square displacement, log the pore temperature, pressure.

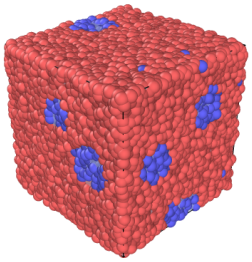

Figure 6: 3d render of the low density script, in the visualization the difference is not really that apparent.

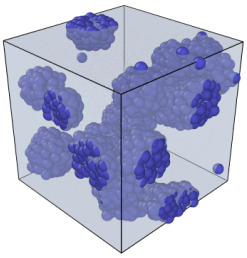

Figure 7: Same internal structure visualization as before, this material had porosity $\phi = 0.08551263$

4 Results

Below are the results from the various simulations performed in this article.

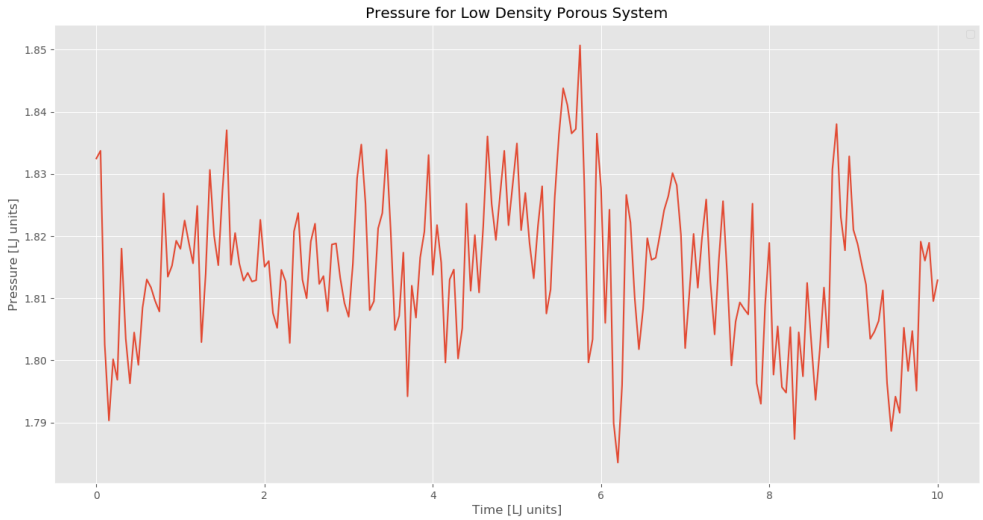

Figure 8: Graph of the pore pressure for the half density randomized pore system

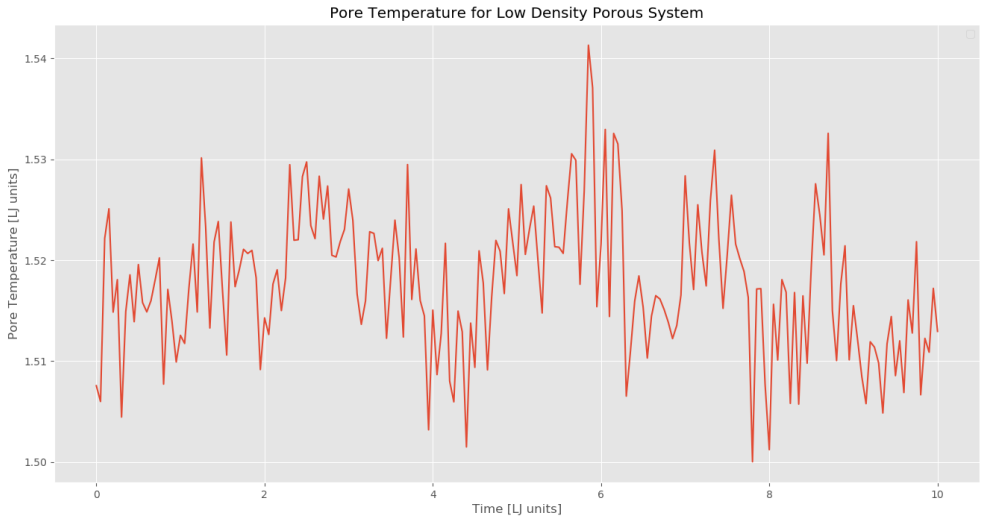

Figure 9: Graph of the pore temperature for the half density randomized pore system.

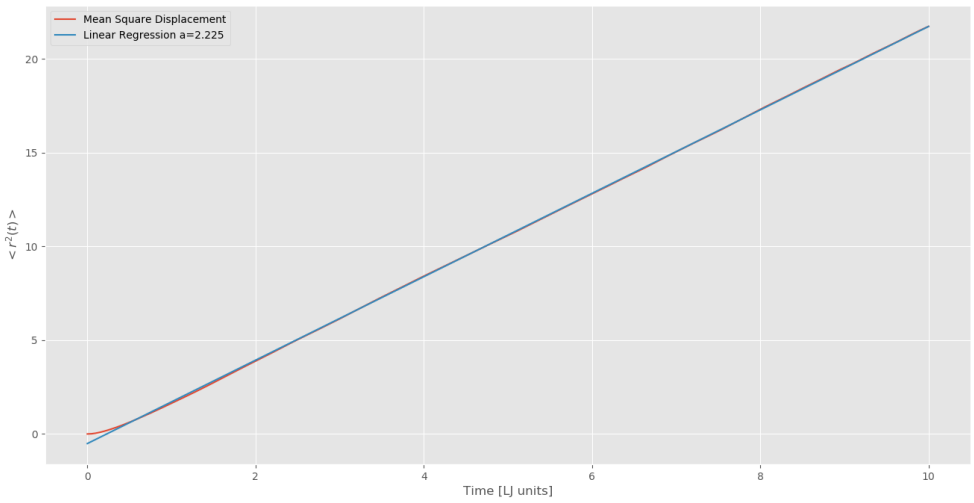

Figure 10: Mean Squared Displacement for the pore group in the half density system. The slope of the graph was found to be 2.225 using scipy's linear regression function.

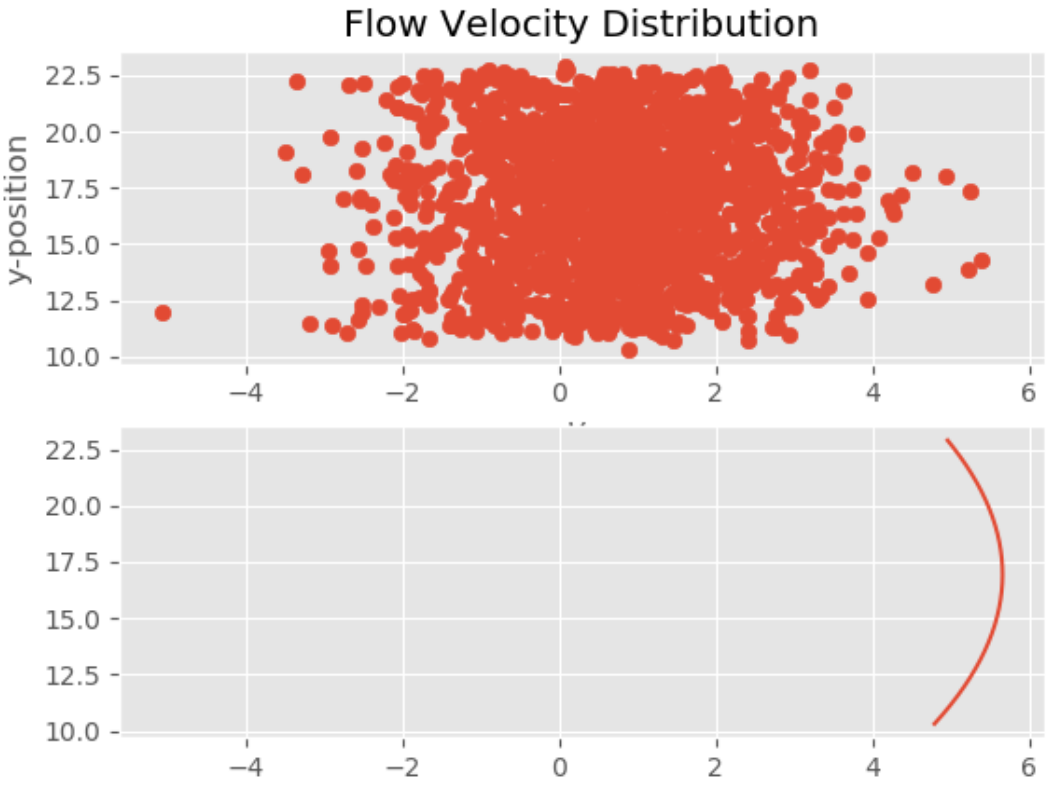

Figure 11: This is a scatter plot and a cubic regression of the x-component of the flow velocity as a function of the y-coordinate. The reader will have to excuse the ugly plot as there was no more time to work on the presentation of the result. This is for a constant force of $F_x = 0.1$.

This velocity distribution is very close to what we expect to see from the continuum solution. The distribution is cubic with center in the middle, however the measurement did not obtain the boundary velocity we expect from the continuum solution with non-slip boundary conditions.

5 Conclusion

In this article we have seen how to generate and simulate nano-porous materials using LAMMPS. Unfortunately due to time constraints I was not able to complete the last task, as I need to move onto the next project now. If given more time more analysis and deeper dives in the relevant background theory could be done.

A Transport Equations

Following is the analogy between Darcy's law, Fourier's law and Ohm's law.

	Darcy's Law	Fourier's Law	Ohm's Law
potential:	p	T	V
current:	$\mathbf{U}$	$\mathbf{q}$	$\mathbf{j}$
transport equation:	$\mathbf{U} = -\frac{k}{\mu}\nabla p$	$\mathbf{q} = -k\nabla T$	$\mathbf{j} = -\sigma\nabla V$
transport coefficient:	k/μ	k	σ

Table 1: Caption

References

[1] Malthe Sørenssen A. Project text; *Introductory molecular modeling*, `https://www.uio.no/studier/emner/matnat/fys/FYS4460/v21/notes/project01-part1to3-v1.pdf`

[2] Feder, J. Flow in Porous Media, University of Oslo, November 8. 2011

[3] Darcy, H. Les Fontaines Publiques de la Ville de Dijon. (Dalmont, Paris, 1856)

[4] Ekstrøm, L. Introductary Molecular Dynamics Modelling, University of Oslo, February 2021.