FYS4460: UNORDERED SYSTEMS AND PERCOLATION ADVANCED MOLECULAR DYNAMICS TOPICS

ALEXANDER HAROLD SEXTON

JUNE 10, 2020

Contents

1. Topic 6: Generating a nano-porous material

Discuss how we prepare a nano-porous matrix with a given porosity in Lammps. How do we characterize the structure of such a material and the dynamics of a fluid in such a material? Provide examples from your own simulations.

- Created nano-porous structures of two types in our projects:
- Cylinders and spheres
- Do this in Lammps by defining N^3 unit cells of length b
- Reduced density: $\rho^* = \frac{n}{(b/\sigma)^3}$
- Initialization of simulation box in Lammps:

```
variable    b       equal 5.72
variable    sigma   equal 3.405
variable    rhostar equal 4/((${b}/${sigma})^3)
variable    nCells  equal 20
units lj
dimension 3
boundary p p p
atom_style atomic
lattice fcc ${rhostar}
region simbox block 0 ${nCells} 0 ${nCells} 0 ${nCells}
create_box 2 simbox
```

```
create_atoms 1 box
```

- Thermalize system at $T = 0.851$

- Cut out a cylindrical shape

- Freeze atoms

```
variable    ymid     equal ${nCells}/2
variable    zmid     equal ${nCells}/2
variable    radius   equal 20/${sigma}
region outside cylinder x ${ymid} ${zmid} ${radius} 0 EDGE side out
region inside cylinder x ${ymid} ${zmid} ${radius} 0 EDGE side in

group moving_particles region inside
group static_particles region outside

set group static_particles vx 0.0 vy 0.0 vz 0.0
fix 1 moving_particles nvt temp ${T0} ${T1} ${Tdamp}
```

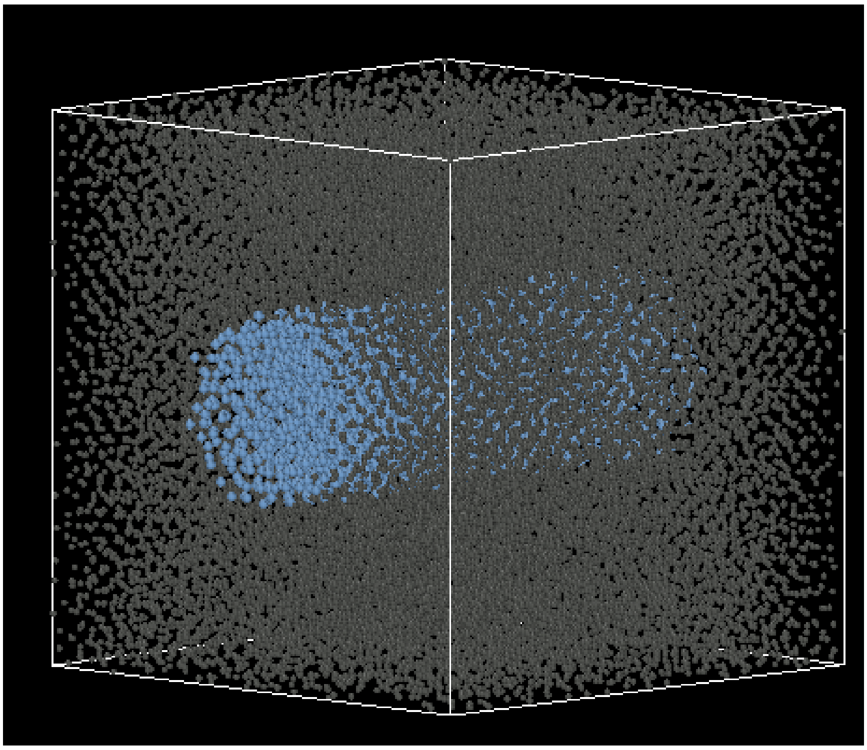

FIGURE 1.1. A cylinder of liquid argon surrounded by static particles.

- Randomly placed spheres

- Initialization in Lammps:

```
variable i loop ${nSpheres}
label loop_shperes
variable r      equal random(${rLow},${rHigh},${seed})
variable x      equal random(0,${nCells},${seed})
variable y      equal random(0,${nCells},${seed})
variable z      equal random(0,${nCells},${seed})

region s${i} sphere $x $y $z $r side in

next i
jump SELF loop_shperes
```

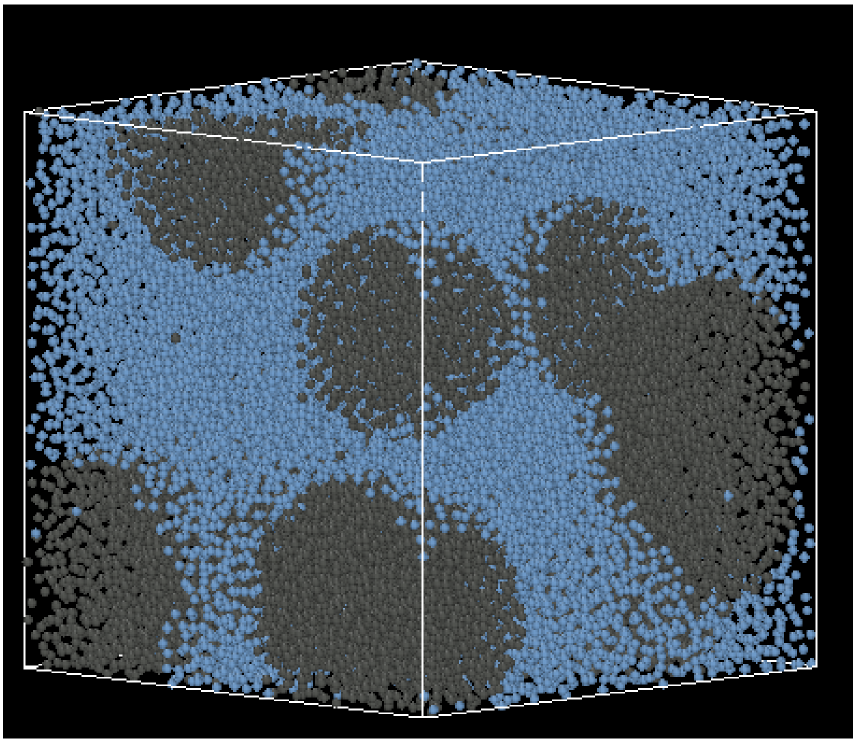

FIGURE 1.2. A nanoporous system of randomply placed spheres.

- Measuring the porosity: $\phi = \frac{V_{space}}{V_{total}}$

```
variable flowing equal count(moving_particles)
variable static equal count(static_particles)
variable phi equal ${flowing}/(${static}+${flowing})
```

- Figure 1.2 shows a system of 20 such spheres.

- Measured porosity: $\phi = 0.45$

- Comparing with theoretical considerations: $\phi_{FCC} = 1 - \frac{\pi}{3\sqrt{2}} \approx 0.26$

- Permeability

- Can be measured by using Darcy's Law for fluid flow: $U = \frac{k}{\mu}(\nabla P - \rho g)$

- Have used simulations of flowing argon to measure permeability as a function of porosity, figure 1.3

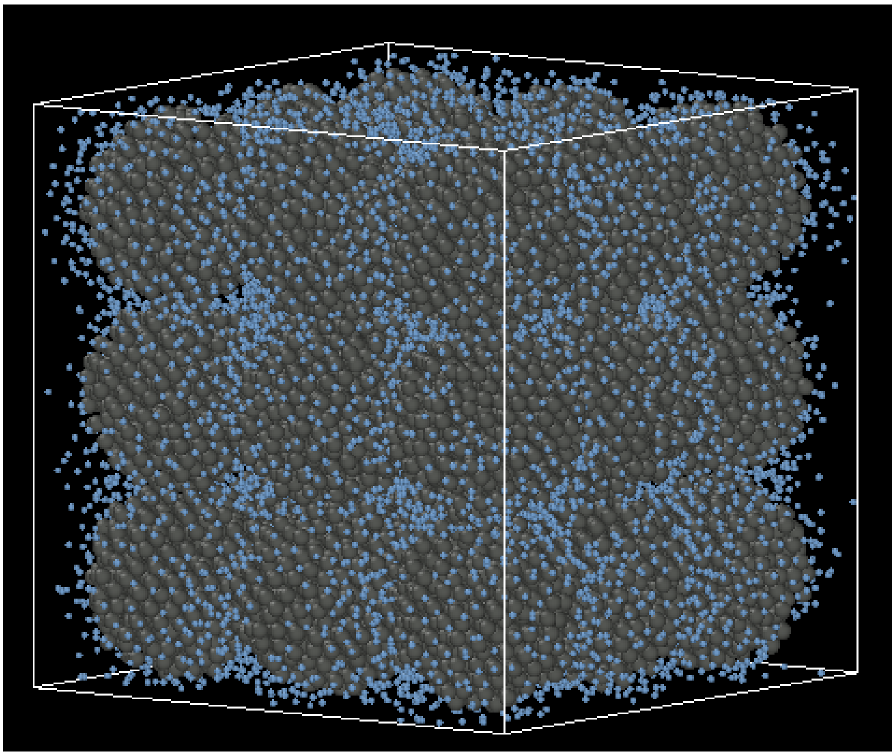

FIGURE 1.3. Visualization of 27 periodically placed solid spheres and flowing argon.

- Compared results with Carman-Kozeny: $k = \frac{a^2}{45}\frac{\phi^3}{(1-\phi)^2}$

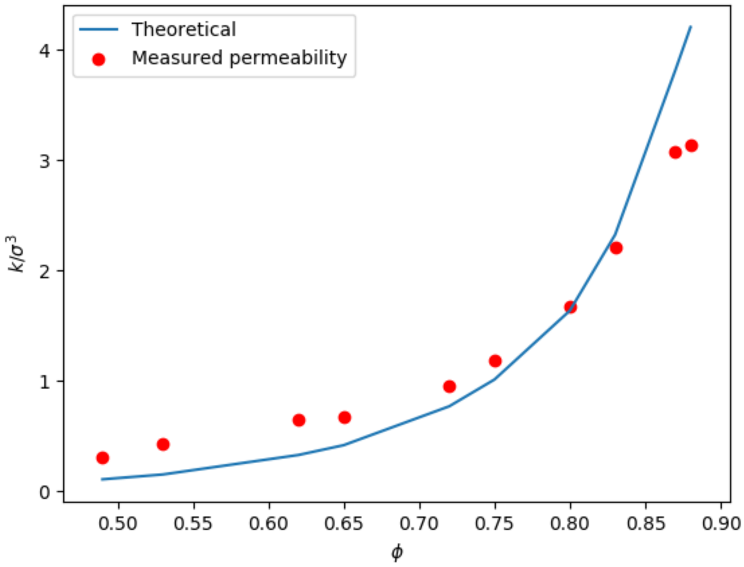

FIGURE 1.4. Caption

2. Topic 7: Diffusion in a nano-porous material

How can you measure the diffusion constant for a low-density fluid in a nano-porous system? Discuss what results you expect. Compare with diffusion in a bulk liquid and in a larger-scale porous medium. Provide examples from your own simulations.

- Definition of diffusion

- Mean squared displacement: $\langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^{N} (\boldsymbol{r}(t) - \boldsymbol{r}(t_0))$

- Measuring MSD in Lammps: `compute msd all msd`

- Diffusion coefficient: $\langle r^2(t) \rangle = 6Dt$

- Considerations when measuring D

- MSD in a bulk liquid

- MSD in a nano-porous media

- Considering density of the fluid

- Results from bulk liquid, density $\rho^* = 0.01$

- Results from nano-porous media, density $\rho^* = 0.003$, $T = 1.5$

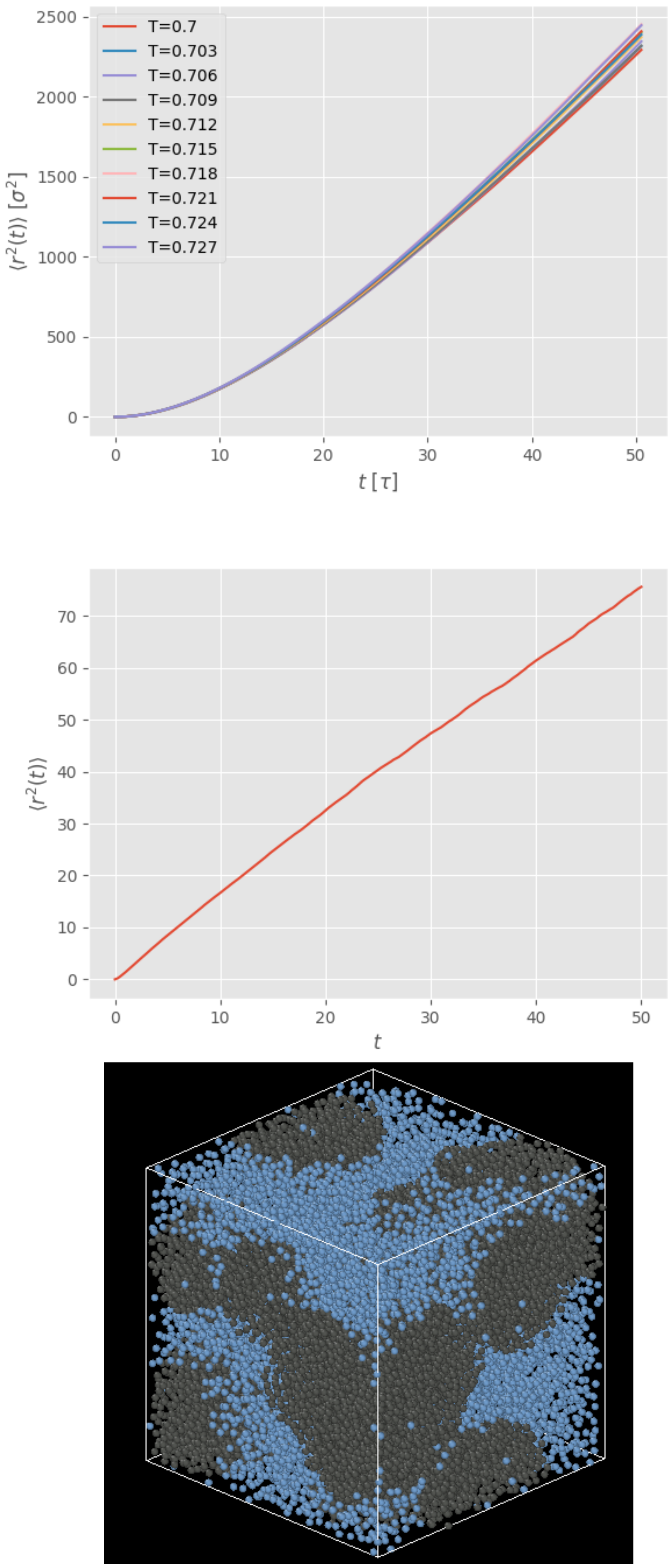

FIGURE 2.1. Mean squared displacement of argon in a bulk liquid (top) and a nanoporous media (mid), depiction of the nanoporous system (bot).

3. Topic 8: Flow in a nano-porous material

Discuss how to induce flow in a nano-porous material. How can you check your model, calculate the fluid viscosity and measure the permeability? What challenges do you expect? Provide examples from your own simulations.

- Introduction of fluid flow in Lammps
- Implemented by `fix 1 flowing_particles addforce 0.1 0.0 0.0`
- Compare results from simulation with continuum mechanics
- Simple hydrodynamic equation for laminar flow
- Derivation: consider a fluid element of size $dx \times dy \times dz$
- Force in x-direction: $p(x)dydz - p(x+dx)dydz$.
- Expect higher velocity near the center of the pipe
- Stress: $\sigma_{xz} = \mu \frac{\partial v_x}{\partial z}$
- Force due to stress: $\mu[\frac{\partial v_x(z+dz)}{\partial z} - \frac{\partial v_x(z)}{\partial z}]dxdy$
- Net force:

$$F_x = p(x)dydz - p(x+dx)dydz + \mu \left[\frac{\partial v_x(z+dz)}{\partial z} - \frac{\partial v_x(z)}{\partial z} \right] dxdy = 0. \tag{1}$$

- Dividing by $dxdydz$:

$$F_x = \frac{p(x) - p(x+dx)}{dx} + \mu \frac{\left[\frac{\partial v_x(z+dz)}{\partial z} - \frac{\partial v_x(z)}{\partial z} \right]}{dz} \tag{2}$$

$$= -\frac{\partial p}{\partial x} + \mu \frac{\partial^2 v_x}{\partial z^2} = 0. \tag{3}$$

- Solution with non-slip boundary conditions:

$$v_x = \frac{1}{2\mu} \frac{\Delta p}{L} (z^2 - a^2), \tag{4}$$

- Compare this result to our simulations
- Liquid argon at $T = 0.851$ with number density $n = 2/b^3$, $b = 5.72$Å in a cylindrical pore
- Force acting on particles: $F = 0.1\epsilon/\sigma$

- Thermalizing considerations

- Record the velocity profile
- Results in 3.1

- Interpreting the result

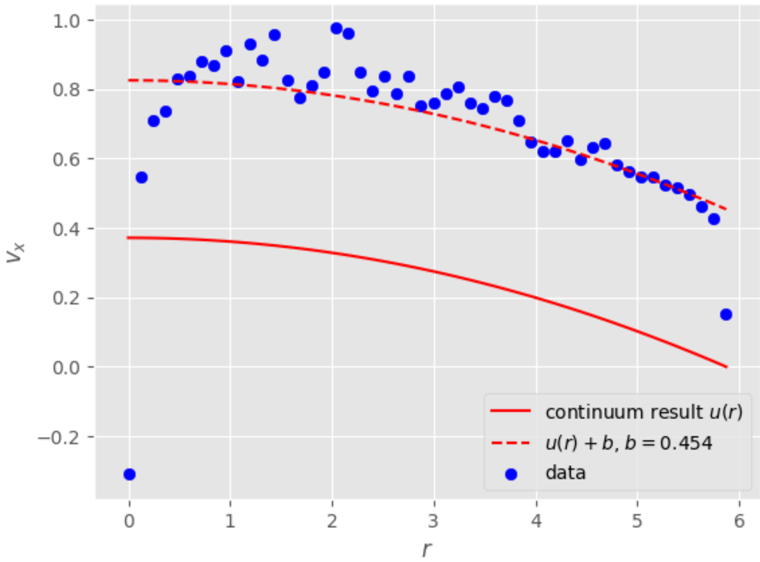

FIGURE 3.1. Velocity profile of liquid argon flowing in a cylindrical pore.

- Estimating the viscosity: $\mu = 0.97\epsilon\tau/\sigma^3 = 86 \times 10^{-6}$ Pa$\cdot$ s

- Estimates from experiment: $\mu = 270 \times 10^{-6}$ Pa$\cdot$s
- Measuring permeability by using Darcy's law: $U = \frac{k}{\mu}\left(\nabla P - nF_x\right)$

- Generate a range of nanoporous materials, figure 3.2

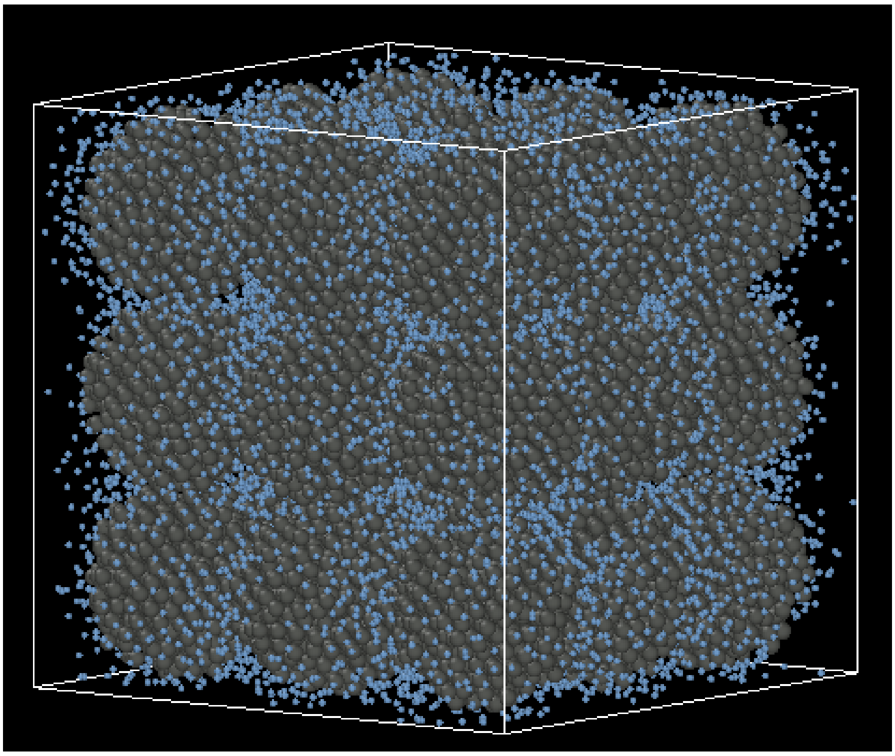

FIGURE 3.2. Nanoporous system of 27 evenly spaced spheres with flowing liquid argon.

- Compare with Carman-Kozeny: $k = \frac{a^2}{45}\frac{\phi^3}{(1-\phi)^2}$
- Results in figure 3.3

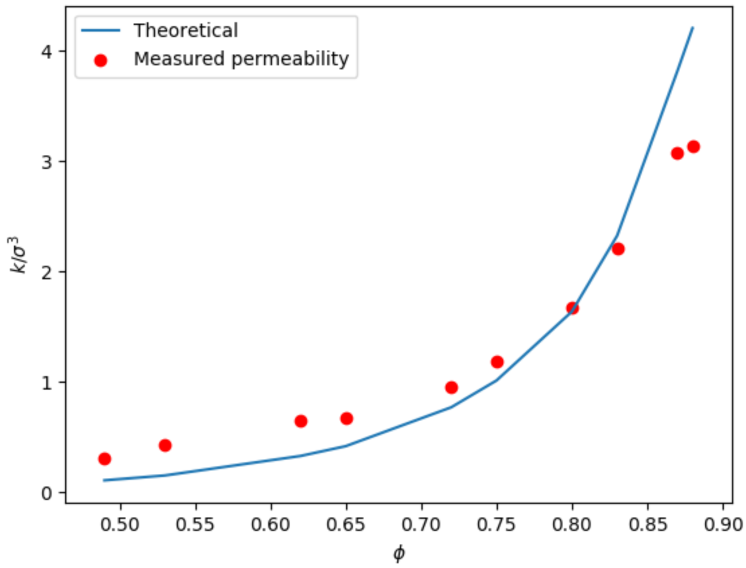

FIGURE 3.3. Permeability as function of porosity in a nanoporous material of spheres.