Mid Semester Project

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Topic: Adsorption

Introduction

A collection of two types of spheres are taken in a simulation box. The first type is a larger sphere of diameter 4D that is centrally located. The other type of sphere of diameter D is distributed in the simulation box randomly with a number density of 0.6. The smaller spheres interact with each other and the larger sphere via pairwise Lennard Jones interactions with a cut-off of 2.5$\boldsymbol{\sigma}$. The LJ parameters are listed as:

$$\epsilon_{1-1} = 0.1 \qquad \sigma_1 = 1.0$$
$$\epsilon_{1-2} = 1.5 \qquad \sigma_{12} = 2.5$$
$$\epsilon_{2-2} = 1.0 \qquad \sigma_2 = 4.0$$

Methodology

A simulation box with periodic boundary is set up to study the adsorption behaviour. The box size is taken to be 20x20x20. The simulation box is divided into two parts by specifying a spherical region of diameter 4 at the centre of the box. The larger sphere is created in this region. The smaller spheres are created outside this region randomly with the help of overlap keyword in create_atoms command of LAMMPS to ensure there is no overlapping atoms which could lead to a lost atoms error. The central atom is fixed in position with the help of fix/setforce command.

After successful set up of the system, it undergoes three processes under the microcanonical ensemble, NVE with a timestep of 0.01.

1. *Initialization run:* The epsilon values are all turned to 1.0 and the system is allowed to run for 10000 steps to reach a state of minimum energy.
2. *Equilibration run*: The pair_coeff command is turned on to the required values and the system starts interacting. It is allowed to reach a state of equilibration for 30000 steps.
3. *Production run:* After reaching a state of equilibration the system is allowed to run for 60000 timesteps.

A dump file is written which outputs the atomic trajectories. This is used for visualization of the atomic positions over time.

The radial distribution function or RDF for type 1 and type 2 atom interactions are calculated which gives an estimate of the particles adsorbed. The RDF shows how the system evolved from the start to the end of the simulation.

Results and Plots:

Initial Setup

The simulation is initialized with the blue smaller spheres distributed in the simulation box with density 0.6 and the red bigger sphere at the centre. For inference and better viewing cut section images have been used for any required demonstration,

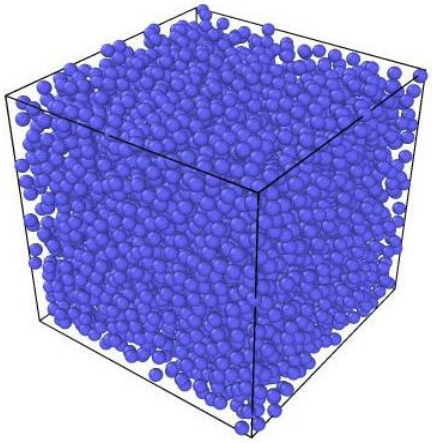
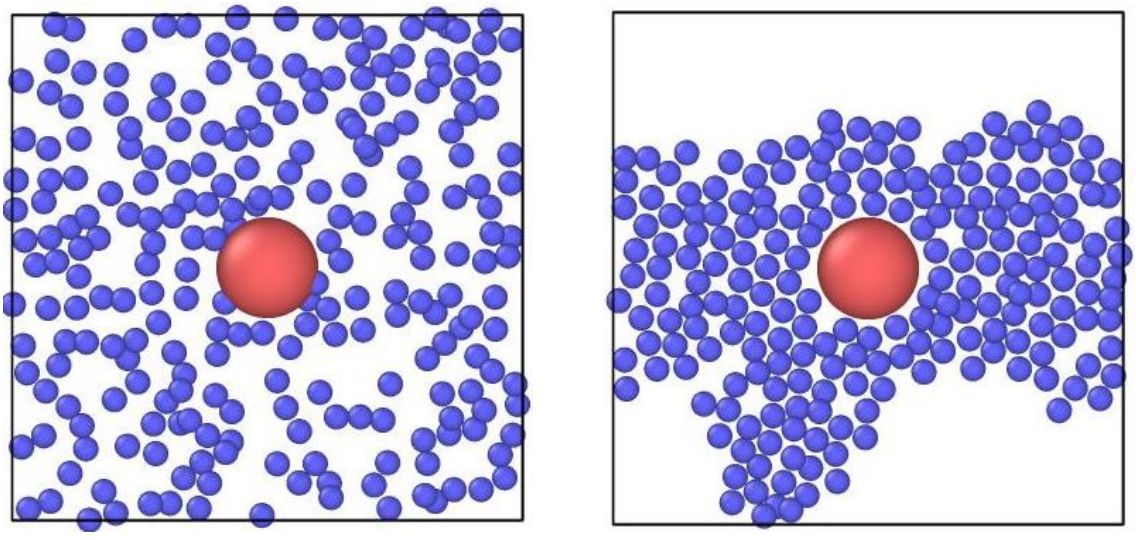


Fig 1: Simulation Setup

Sample Output Trajectories

OVITO is used for reading and visualization of the phase space trajectories with the help of the dump file written as output by LAMMPS. A cut section view is taken to show the development of atomic positions.

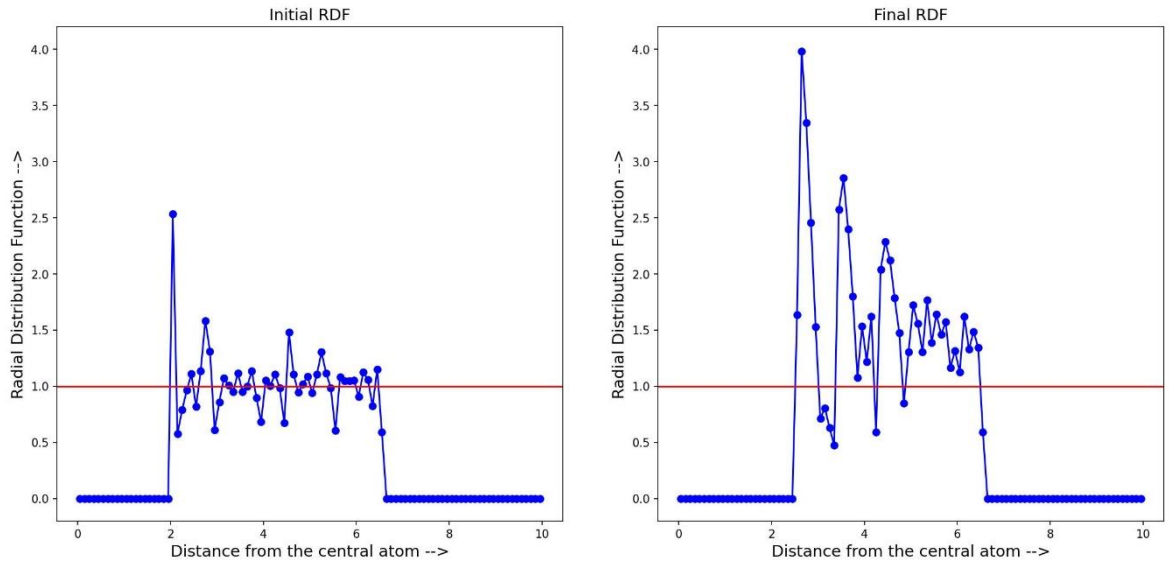


(a) (b)

Fig 2: (a) Cut section view showing initial position at the start of the simulation and (b) Cut section view showing final position of the atoms at the end of the simulation.

Property Labelled Plots

The RDF files written as input are read by Python and plots it as shown. The RDF is integrated between 2 and 3 to get the count of the nearest neighbours.



(a) (b)

Fig 2: (a) Initial RDF at the start of the simulation and (b) Final RDF at the end of the simulation.

Discussion

Visualizing the dump file with OVITO shows that adsorption takes place and the smaller spheres crowd around the larger sphere. RDF also shows that at the end of the simulation the density around the larger sphere is significantly higher. Integrating the RDF between a distance of 2.5 to 3 units from the centre of the larger sphere gives us an estimate of the number of nearest neighbours. Taking a projected area of πD^2 on the surface of the sphere gives us an estimate of the surface area of the larger sphere covered by the smaller spheres.

$$N = \int_{r_1}^{r_2} n\, g(r) 4\, \pi\, r^2\, dr$$

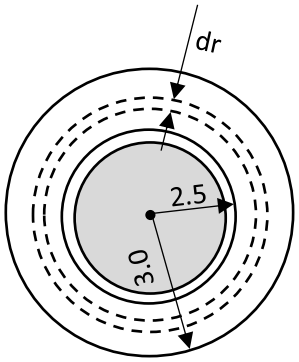


Fig: 3 Integration limits for RDF calculations

Here,

n = number density = 0.6 (specified in the problem statement)

g(r) = RDF of smaller spheres surrounding the larger sphere.

$4\pi\ r^2\ dr$ = Infinitesimal volume of a spherical shell surrounding the larger sphere.

r_1 = 2.5 (Distance where smaller spheres are most stable)

r_2 = 3 (Distance upto which the first shell is considered. This shell can accommodate only 1 layer of smaller spheres around the larger spheres.)

Integrating we get N= 27 spheres initially

Therefore, projected area on sphere = $27 * \left(\frac{\pi}{4} * 1\right)$

$= 6.75\ \pi = 21.2058$

Surface area of the sphere at 2.5 units = $4*\pi*(2.5^2)$

$= 78.539$

Percentage surface area covered initially = $\frac{21.2058}{78.539} * 100$

= **27 %**

Integrating RDF at the end of simulation, we get N as 64

Therefore, projected area on sphere = $64 * \left(\frac{\pi}{4} * 1\right)$

$= 16\ \pi$

$= 50.2656$

Surface area of the sphere at 2.5 units = $4*\pi*(2.5^2)$

$= 78.539$

Percentage surface area covered = $\frac{50.2656}{78.539} * 100$

= 64 %

Conclusion

The LJ interaction between the larger sphere and smaller spheres has a stronger attraction as specified in the pair_coeff command of the LAMMPS input script, due to which the smaller spheres get adsorbed on the surface of the larger sphere. This is evident by visualizing the phase space trajectories written into the dump file and rendered with OVITO. Finally, the RDF plotted at the beginning of the simulation when integrated shows 27 spheres as the nearest neighbours of the larger sphere. Over the simulation this number increases to 64 which confirms that adsorption has indeed taken place.

References:

- https://docs.lammps.org/Manual.html
- https://www.ovito.org/manual/