

**Programming project report 3: Liquid equilibration***Submitted by Mikhail Ivanov***Introduction**

For this part of the programming project, the radial distribution function (RDF) calculation is implemented as a separate program from the main molecular dynamics (MD) code. The RDF calculation program reads the output trajectory file, saved by the main MD code and produces an output file with the RDF data. It is possible to choose between the calculation of RDF for one timestep of the trajectory, and the calculation of the time-averaged RDF for any part of the input trajectory, excluding the equilibration part of the trajectory. RDF data is then plotted with a separate *Python Matplotlib* script.

Besides the RDF calculation, it is now possible to control the system's temperature to a certain degree by scaling the velocities to the input temperature for an arbitrary number of timesteps (though 1 picosecond is usually enough for the simulated system). After the equilibration period, the scaling of the velocities is disabled, and the system's temperature continues to fluctuate around the input temperature. All the system's averages are collected after the equilibration period.

Moreover, one may control the density of the system now. The desired density is specified in the input file for the main MD code. During the initialization of the MD simulation, the starting lattice and the simulation box is scaled to achieve that density.

Two 40 ps long simulations with 4 fs timestep were carried out for the system of 1000 argon atoms: at  $T = 95$  K and  $\rho = 1374$  kg/m<sup>3</sup>, and at  $T = 130$  K and  $\rho = 1160$  kg/m<sup>3</sup>. For every step of the first 300 steps (correspond to 1.2 ps of the simulation time) velocities were scaled to achieve the desired temperature. Input temperatures and densities match with those used in the simulations in the Rahman (1964) paper, so it is possible to compare the results as well as study the differences of RDFs between two systems. The properties of the simulated systems (RDFs, kinetic, potential and total energies and temperatures) were studied to determine their behavior during and after the equilibration.

**Theory***1. Radial distribution function*

For a system of  $N$  identical particles, the radial distribution function (or the pair-correlation function) shows the correlations in positions of the particles in the system. If the particles interact with each other, for example via the Lennard-Jones potential (or any other potential), each particle creates a specific local environment that involves the changes in local particle densities around it.

RDF -  $g(r)$ , can be expressed in the following equation:

$$g(r) = \frac{n(r)}{4\pi r^2 \Delta r} \cdot \frac{V}{N}$$

where  $4\pi r^2 \Delta r$  is the volume of the spherical layer of radius  $r$  and width  $\Delta r$ ,  $n(r)$  is the number of particles in the spherical layer,  $V$  – is the total volume of the system, and  $N$  is the total number of particles in the system. The first part of the expression can be interpreted as a local particle density in the spherical layer  $[r, r + \Delta r]$  and the second part is the inverse average particle density. In other words, the RDF is the ratio of local density to the average density.

RDF describes the structure of the local environment around each particle in the system. For crystalline solids, RDF has multiple narrow peaks, and between them, the function approaches zero as the structure is very ordered and the particles can only oscillate around the lattice sites. For the liquids and glasses, one often sees high RDF peak at small values of  $r$ , but with increasing separation, the peaks become lower and wider until the correlation disappears completely after several peaks with the RDF approaching unity (average particle density). This is because these systems are ordered only on small distance scales, close to the interatomic distances. For real gases, the rate of correlation decay is even higher than for the liquids and glasses, and for the ideal gases (no interaction between the particles) the RDF is a constant equal to unity, as there are no correlations in positions of ideal gas particles.

It is possible to derive RDFs from both experimental techniques (for example neutron scattering) and simulations, like molecular dynamics or Monte-Carlo. Thus, the calculation of RDFs is a very powerful tool for simulations, as it can be used to test the method or the forcefield and compare the results with the experimental data.

## 2. Equilibration

Equilibrium is a fundamental concept of thermodynamics. The most common definition of the equilibrium involves the description of a system in the state of equilibrium – any thermodynamical property (temperature, pressure, chemical potential, etc.) for the system in the equilibrium is identical for any part of the system as well as there are no flows of matter or energy to the system or out of it. The large part of the thermodynamics was designed for the systems in the equilibrium state.

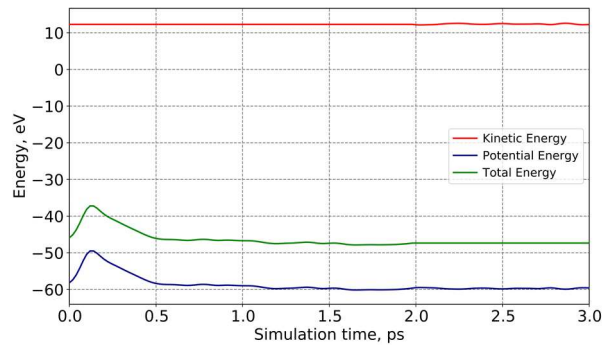
That means that many thermodynamical properties of any system could be obtained when the system is in the equilibrium state. That is why in simulations one tries to drive the system to the equilibrium state as close as possible. However, the thermodynamic properties of simulated microscopic systems are not constant like for the macroscopic systems, because the contribution of each particle is not negligible. The properties of the microscopic systems in equilibrium are fluctuating around the mean value, but do not drift away from it. Thus, from a practical point of view, one should simulate the system long enough to obtain non-drifting properties.

## Results

### 1. Properties of the system during equilibration

For this part of the results section, the first few picoseconds of the trajectory of the system of 1000 argon atoms at  $T = 95$  K and  $\rho = 1374$  kg/m<sup>3</sup> was examined to obtain information about its equilibration.

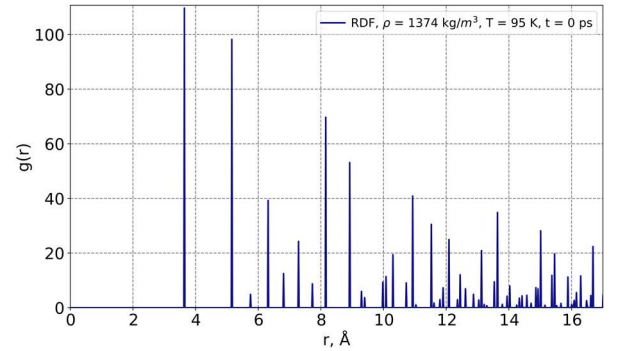
It is quite easy to follow the changes in the energies of the system during the simulation. Kinetic, potential and the total energies of the simulated system against the simulation time are presented in *Figure 1*:



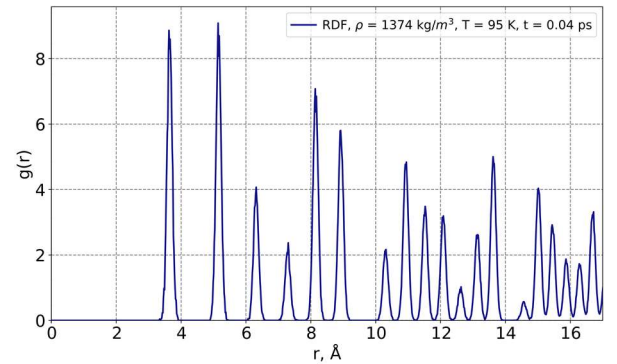
*Figure 1 – Kinetic, potential and the total energy of the simulated system at first 3 ps. Equilibration period (velocity scaling) is 2 ps.*

For the first 2 ps of this simulation, the velocity of each particle is scaled to achieve the desired temperature. As the system starts from the lattice, it should take some time to be able to transform into the liquid state. One can see the peaks of potential energy and the total energy around 0.2 ps of the simulation time, but they flatten quickly and approach constant value at some point between 1.0 and 1.5 ps. Even after the disabling of velocity scaling after 2 ps, the total and potential energies stay almost the same.

Moving to the RDFs (*Figures 2-6*) – at the starting point ( $t = 0$  ps) one can see high multiple narrow peaks, which is typical for crystalline solids. At  $t = 0.04$  ps the latter peaks become wider, at  $t = 0.4$  ps the RDF resembles liquid structure, but with noticeable higher order peaks. However, after  $t = 0.8$  ps, RDF doesn't change very much and appears to be typical RDF of the Lennard-Jones fluid.



*Figure 2 – RDF at  $t = 0$  ps*



*Figure 3 – RDF at  $t = 0.04$  ps*

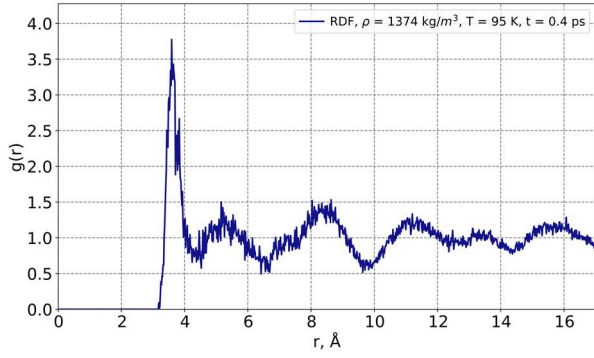


Figure 4 – RDF at  $t = 0.4$  ps

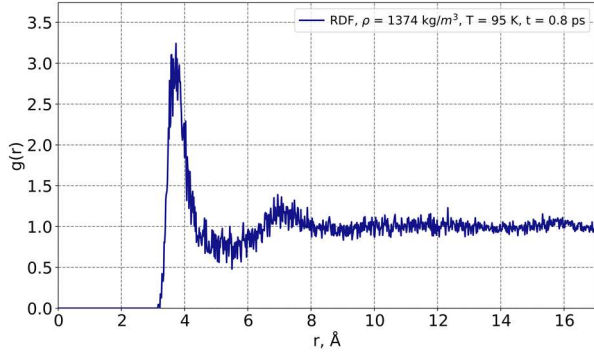


Figure 5 – RDF at  $t = 0.8$  ps

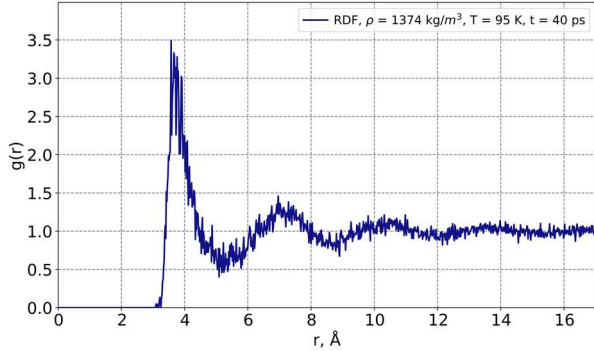


Figure 6 – RDF at  $t = 40$  ps

The present data suggest that the equilibration of the system of 1000 argon atoms at  $T = 95$  K and  $\rho = 1374$  kg/m<sup>3</sup> occurs roughly at 0.8-1.5 ps simulation time interval. Equilibration in the system at  $T = 130$  K should last for even less time, as the velocities of the particles are higher, and the system can move away from the starting lattice state faster. For the future simulations, the velocity scaling (equilibration) period was set to 1.2 ps.

## 2. Properties of the system at apparent equilibrium state

Energies, temperature and RDFs, obtained from the last 38.8 ps of the trajectory (1.2 ps is the equilibration period, 40 ps is the total simulation length) are plotted

for the last part of the results section. On Figures 7 and 8, the kinetic, potential and total energies are plotted for two simulated systems at 95, and 130 K. Total energies stay the same, kinetic and potential energies fluctuate around the mean value for both cases.

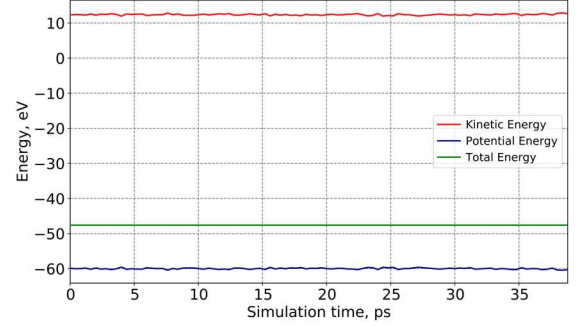


Figure 7 – Kinetic, potential and the total energy of the simulated system at  $T = 95$  K. Equilibrated part of the trajectory is shown.

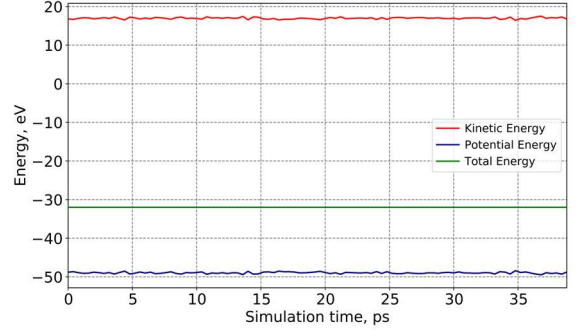


Figure 8 – Kinetic, potential and the total energy of the simulated system at  $T = 130$  K. Equilibrated part of the trajectory is shown.

On Figures 9 and 10 the systems' temperatures are shown. While they are fluctuating greatly, no significant drift is present, and the mean temperatures are very close to the initial ones (95.8 and 131.3 K, respectively).

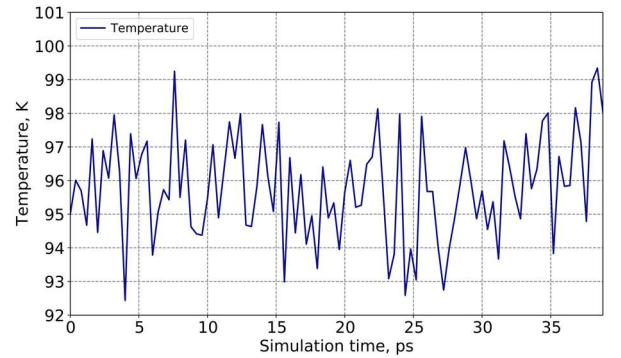


Figure 9 – Temperature of the system with  $T = 95$  K as the initial desired temperature. Equilibrated part of the trajectory is shown.

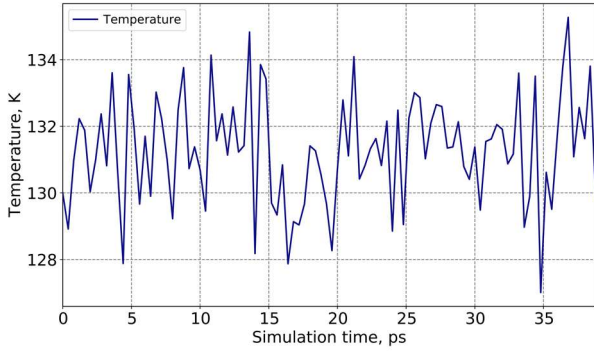


Figure 10 – Temperature of the system with  $T = 130$  K as the initial desired temperature. Equilibrated part of the trajectory is shown.

On Figure 11, one can see two RDFs for the both systems on one graph. Three noticeable RDF peaks are present for the system at  $T = 95$  K, while only two are present for the system at the higher temperature. In general, peaks of the high temperature RDF are lower and wider which is because the particles have more kinetic energy, so they are less susceptible to the local potential minima. The positions of the peaks of the low temperature RDF are match the results published in the Rahman (1964) paper.

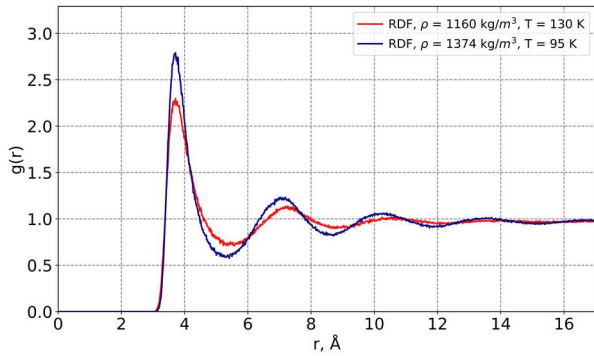


Figure 11 – Time-averaged RDFs for the systems at 95 K (blue line) and 130 K (red line). Averaging over last 38.8 ps is performed.

Finally, the first coordination number was obtained for both systems. The first peak of the RDF indicates a relatively strong short-ranged correlation of the particles' positions due to the formation of the local environment, that is often called the 'coordination sphere'. It is possible to calculate the number of particles –  $n(r)$ , residing in such coordination sphere:

$$n(r) = \int_{r_i}^{r_k} 4\pi r^2 \frac{N}{V} g(r) dr$$

Where  $r_k - r_i$  is the width of the RDF peak (for the first coordination sphere  $r_i = 0$ ,  $r_k$  - location of the first RDF minimum).

With the finite  $\Delta r$  the integral transforms to the following sum:

$$n(r) = \sum_{r_i}^{r_k} 4\pi r^2 \frac{N}{V} g(r) \Delta r$$

The RDF and the cumulative coordination number for the system at  $T = 95$  K are shown in Figure 12.

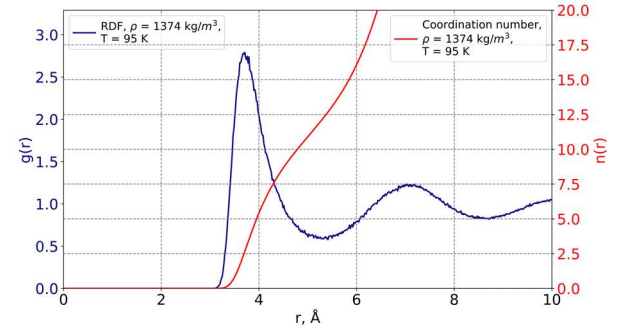


Figure 12 – Time-averaged RDF of the system at 95 K (blue line) and the corresponding cumulative coordination number (red line). Averaging over last 38.8 ps is performed.

For the system at 95 K, the first RDF minimum is located somewhere between 5.14 and 5.51 Å which corresponds to the value of the first coordination number from 11.5 to 13.0. At 130 K, the minimum located a bit further, approximately from 5.22 to 5.66 Å with corresponding coordination number from 10.0 to 12.1. It seems reasonable that at higher temperatures the first coordination sphere is more sparsely populated as the higher temperature destabilize the local structure.

## Conclusion

The implementation of the radial distribution function allows investigating the structural properties of the Lennard-Jones fluids. It was shown, that for two simulated systems, containing 1000 argon atoms at  $T = 95$  K and  $\rho = 1374$  kg/m³, and at  $T = 130$  K and  $\rho = 1160$  kg/m³ equilibration lasts for approximately 1 picosecond, as the energies and the RDFs become stable after that time. From the computed RDFs, it is possible to conclude that the system with higher temperature is more disordered than the system with lower temperature.

The code is attached via Athena.