

Exercise 3 for 'Computational Physics - Material Science', SoSe 2025
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Please provide a well documented submission of your solution. Your submission should include

- A pdf file containing the solution to the questions with the corresponding equations that are implemented in your codes. Figures must contain axis titles with corresponding units and a caption.
- The source code should be commented, and the equations given in the pdf file have to be referenced in the source code.
- There is no need to provide the trajectory files.
- In case your code is not working properly, please provide a description of the debugging attempts you did.

Exercise 3.1: The radial distribution function, RDF

The structure of simple fluids can be characterized by the Radial Distribution Function (RDF), $g(r)$. This function gives the probability of finding a pair of atoms at a distance r relative to the probability expected for a totally random distribution at the same particle density. In computer simulations employing pair potentials, $g(r)$ can be computed as

$$g(r) = \frac{V}{N^2} \left\langle \sum_i \sum_{j(j \neq i)} \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle \quad (1)$$

where $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ is the distance vector between atoms i and j , \mathbf{r} is the vector with respect to the position coordinates of one atom, $r = |\mathbf{r}|$, and V and N are the volume of the simulation box and the number of atoms in the simulation box, respectively. The objective of this exercise is to calculate and analyze the RDF of a LJ fluid in 3D. [The $\langle \dots \rangle$ average in eq. (1) has to be interpreted as time average in your simulations.] The RDF can be calculated using the following numerical recipe:

- Each $N_{analyze} \approx 10$ steps of the production run, calculate the distance r_{ij} between atoms i and j , and sort these distances, in a cumulative way, into a histogram where each bin size is δr . When sorting into the histogram, only consider r_{ij} smaller than half the box-length, and keep track of the number of analyzed configurations in N_{gr} .
- At the end of the production run, calculate the average number of atoms in each bin b according to $n(b) = n_{bin}(b)/(N N_{gr})$ where $n_{bin}(b)$ is the number of atoms in the b bin of the histogram, as well as the average number of atoms in the same bin in an ideal gas, $n^{id}(b)$, at the same density ρ according to $n^{id}(b) = \frac{4\pi\rho}{3}[(r + \delta r)^3 - r^3]$.
- The RDF is $g(r + \frac{1}{2}\delta r) = n(b)/n^{id}(b)$.

- Make sure that the RDF converges to 1 at large distance.
- Increase the dimensionality of your MD engine implemented in 2D in exercise 2.1 to 3D. This operation can be done by (i) initializing the atoms' position and velocity along the z-direction, (ii) calculating the force along the z-direction using the minimum image convention, and (iii) implementing the time integration along the z-direction. Construct a simulation setup consisting of $N = 512$ atoms distributed on a 3D lattice such that the number density is $\rho = N/V = 0.01\sigma^{-3}$. Initialize the atom velocities to obtain a temperature $T_0 = 300K$. The atoms are interacting through a LJ potential, with $\epsilon = 0.297$ kcal/mol and $\sigma = 0.188$ nm. Equilibrate the system by simulating for time t_{eq} using a timestep Δt (provided below). For efficient equilibration, rescale the velocities of atoms to the desired temperature T_0 every 10 steps. After the equilibration run, perform a production run during t_{prod} , and report the mean potential energy obtained during the production run. (7 points)
 - Enrich the 3D MD implementation with a function that calculates, on-the-fly, the RDF, $g(r)$. Using the same setup as in a), calculate the RDF obtained during the production run. Plot the result, and compare your data to the theoretical prediction of the $g(r)$ in the low density limit. (5 points).
 - Using the methodology given in a) and b), calculate and plot $g(r)$ but now with $\rho = 0.5\sigma^{-3}$. At which distance, r , do you find the maximum peak? What is the height and the meaning of this peak? What is the size of the first solvation shell, defined by the first minimum (disregarding the global minimum at $r = 0$)? (4 points)
 - The potential energy per particle can be calculated by

$$U/N = \frac{\rho}{2} \int_V d\mathbf{r} V_{LJ}(r) g(r),$$

Does the result agree with your result from direct averaging of \hat{U} obtained in a) and c)? The $V_{LJ}(r)$ is the pair potential (including cutoff) you are using. What is the deviation and where could it come from? (4 points) [With $d\mathbf{r}$ in the integral we denote an integral over 3D space.]

- [optional]** The isothermal compressibility, κ_T , can be calculated from $g(r)$ using the compressibility equation and the Kirkwood-Buff integral, which writes

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = \frac{1}{k_B T_0 \rho} + \frac{1}{k_B T_0} \int_V d\mathbf{r} [g(r) - 1],$$

where p is the internal pressure of the system. Calculate the isothermal compressibility, κ_T , for your system from the integral on the right hand side. What is the change of the isothermal compressibility when decreasing the number density from $0.5\sigma^{-3}$ to $0.01\sigma^{-3}$? (4 points)

Numerical values of quantities representative of Argon:

quantity	value (units)
k_B	0.0019849421 (kcal/mol/K)
ϵ	0.297741315 (kcal/mol)
σ	0.188 (nm)
T_0	300 (K)
m	39.95 (g/mol)
Δt	1 (fs)
t_{eq}	10000 Δt
t_{prod}	20000 Δt