Universität Freiburg – Institut für Physik
Applied Theoretical Physics
Prof. Dr. J. Dzubiella

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Exercise 9 for '*Computational Physics - Material Science*', SoSe 2021
Email: adnan.gulzar@physik.uni-freiburg.de, sebastien.groh@physik.uni-freiburg.de
Tutorials: Dr. Adnan Gulzar and Dr. Sebastien Groh

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 9.1: Dynamics of a molecular system

In classical Molecular Dynamics, M molecules, indexed $m_i = 1..M$, are defined as a set of n atoms per molecule that are held together by simple elastic forces. Hence, the force field replaces the true potential with a simplified model. The total number of atoms is then $N = Mn$ which we can index for convenience with $i = 1..N$. For dimers, i.e., $n = 2$, thus $m_1 = 1, m_2 = 1, m_3 = 2, ..,$ and a typical expression for the force field is:

$$U = \sum_i \sum_{j, m_i = m_j} \frac{k_b}{2}(r_{ij} - r_0)^2 + \frac{1}{2}\sum_i \sum_{j, m_i \neq m_j} U_{LJ}(r_{ij})$$

where the first term refers to the intramolecular 'bond' contribution to the total energy, and r_{ij} is the distance between the two connected atoms of the same molecule, i.e., $m_i = m_j$. (It is typically written as the sum over 'bonds'.) k_b and r_0 represent the bond strength and the equilibrium bond length, respectively. The second term serves to describe the known LJ interaction between all atoms, excluding interactions between atoms of the same molecule. The objective of this exercise is to (i) implemented bonded potential to describe simple molecules, and (ii) calculate the self-diffusion coefficient of a molecular system.

a) Let us assume a N_2 (di-nitrogen) molecule defined by its bond length, $r_0 = 1.07$ Å, and its bond strength, $k_b = 410020$ kJ/mol/nm^2. The mass of the N-atom is 2.32e-26 kg. Calculate and plot the time evolution of the bond length, $r(t)$, versus t of a single di-nitrogen molecule with an initial bond length of 1.1 Åand no initial velocity. What is the corresponding vibration frequency, and how does it compared with the analytical solution?

b) Starting with the implementation of the LJ fluid in the canonical ensemble as discussed in Exercise sheet #6, modify your code to simulate a molecular system made of molecules of

di-nitrogen for which both intermolecular and intramolecular interactions are considered. The equilibrium bond length can be considered to build the initial configuration, and the M molecules can be distributed on a regular lattice as initially done with the LJ fluid. Generate the trajectory of a system containing $M = 6^3$ di-nitrogen molecules included in a simulation box of volume V such that the number density of di-nitrogen molecule is $\rho = M/V = 0.05\sigma^{-3}$ at a temperature $T_d = 300$ K for 40000 time steps (2000 time steps for the equilibration run, and 38000 time steps for the production run). Repeat the same calculation but now with $\rho = M/V = 0.25\sigma^{-3}$. For each trajectory, calculate and plot the mean bonds length obtained during the production run. Calculate and plot the radial distribution function, $g(r)$ for (i) the molecular system, and (ii) the atomic system. Provide an ovito snapshot of the molecular system at the end of the production run.

c) Using the trajectories obtained in (b), calculate and plot the mean-squared displacement, $< \Delta r^2(t) >$ versus t of the N_2 molecules defined as:

$$< \Delta r^2(t) >= \frac{1}{M} \sum_m (r_m(t) - r_m(t=0))^2$$

where M is the number of di-nitrogen molecules, and $r_m(t)$ is the position of the center-of-mass of molecule m at time t. What is the coefficient of self-diffusion of the N_2 molecules in the gas and liquid phases? Compare to available experimental data for N_2 in the gas and liquid phases and discuss.

Numerical values of quantities to be used:

quantity	value (units)
k_B	1.38×10^{-23} (m^2 kg s^{-2} K^{-1})
ϵ	0.1 k_BT
σ	3.26×10^{-10} (m)
T_d	300 (K)
mass	2.32×10^{-26} (kg)
r_0	1.07 (Å)
k_b	410020 (kJ/mol/nm^2)
Δt	0.5×10^{-15} (s)