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

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Exercise 6 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 6.1: Equation of State

The objective of this exercise is to enrich the NVT engine implemented in the previous exercise with a routine that evaluates the pressure, P, of the system through the internal virial. Once implemented and validated, the equation of state, P versus density ρ, of a LJ fluid is calculated.

The *internal* virial, ϑ, is defined as

$$\vartheta \equiv \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{f}_i = \sum_{i=1}^{N} \sum_{j>i} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij}$$

where $\mathbf{f}_i$ is the total force acting on the i-th atom, $\mathbf{f_{ij}} = -\frac{\mathrm{d}U(r_{ij})}{\mathrm{d}\mathbf{r_{ij}}}$ is the force acting between atoms i and j because of pair potential, U, and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. Either of the expressions above can be used to calculate ϑ from simulations. With periodic boundary conditions (PBC), the following should be carefully considered:

- $\mathbf{r}_i$ is the *PBC-wrapped* (that is, minimum image) coordinate of particle i.
- $\mathbf{r}_{ij}$ is the *PBC-wrapped* distance vector between particles i and j.

Following Clausius, the pressure, P, is related to the kinetic energy, K, the volume, V, and the internal virial through

$$P = \frac{1}{3V}\left(2K + \vartheta\right),$$

which can be used to calculate both the instantaneous pressure $P(t)$, as well as the average pressure $\langle P \rangle$ (= $\langle P(t) \rangle$) in numerical simulations. The angular brackets here denote time-averaging.

a) Enrich the 3D MD implementation of Exercise sheet #5 with a function that evaluates the pressure, P, of the system. Simulate, during 50000 time steps, the trajectory of a system containing 8^3 atoms included in a simulation box of volume V such that the number density $\rho = N/V = 0.5\sigma^{-3}$. The temperature of the system is equilibrated and maintained at $T_d = 300K$ using a NH thermostat. The characteristic time, t_c, of the NH thermostat is $t_c = 50\delta t$ where δt is the simulation time step. The first 5000 time steps are used for the equilibration of the system, and the last 45000 time steps are for the production run. Analyze the trajectory by plotting $P(t)$ and $T(t)$ versus t, and $g(r)$ versus r obtained during the production run. Decompose the production run in 9 blocks of 5000 time steps, and calculate the mean pressure, $\langle P \rangle$, the isothermal compressibility, κ_T (as defined in exercise sheet #3), and the heat capacity, C_V (as defined in exercise sheet #5) for each block. Calculate and report the corresponding statistical error for $\langle P \rangle$, κ_T, and C_V.

b) Repeat the calculations and analysis as in (a) but now with $\rho \in (0.1\sigma^{-3}, 0.05\sigma^{-3}, 0.01\sigma^{-3}, 0.005\sigma^{-3})$. The ideal gas pressure, P_{id}, at a given temperature, T_d, is given by $P_{id} = \rho k_B T_d$. Plot the deviation of the calculated pressure, P, from the P_{id} as a function of ρ. Does $P - P_{id}$ vary linearly with ρ? Comment on your observations, and provide justification using physical insights.

Numerical values of quantities to be used:

quantity	value (units)
k_B	1.38×10^{-23} (m^2 kg s^{-2} K^{-1})
ϵ	$0.5\ k_B T_d$
σ	2.55×10^{-10} (m)
T_d	300 (K)
mass	105.52×10^{-27} (kg)
Δt	10^{-15} (s)
t_c	$50\ \Delta t$ (s)
ρ	$\in [0.005 : 0.5]$ (σ^{-3})