Universität Freiburg – Institut für Physik
Applied Theoretical Physics
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Exercise 4 for '*Computational Physics - Material Science*', SoSe 2025
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Tutorials: Andreas Doell and 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 4: External Fields: Confined LJ Fluid Between Two Walls

Let us consider the 3D space divided in two regions. The region (half space) defined by $z < 0$ is occupied by a homogeneous solid (continuum), while an atom is located at $z = z_f > 0$. The total interaction energy between the solid and the atom, U_{wall}, is of the 9-3 LJ form (will be justified in the lecture):

$$U_{\text{wall}}(z_f) = \frac{3\sqrt{3}}{2}\epsilon_{\text{wall}}\left[\left(\frac{\sigma_{\text{wall}}}{z_f}\right)^9 - \left(\frac{\sigma_{\text{wall}}}{z_f}\right)^3\right],$$

where σ_{wall} and ϵ_{wall} describe the characteristics of the wall-atom interaction. The interaction acts on the atoms within a cut-off distance, $z_{\max} = 2.5\sigma_{\text{wall}}$, in the direction normal to the wall. Such an approach is commonly used to model the interactions between a structureless ('coarse-grained') solid wall and a liquid.

The objective of this exercise is to simulate a LJ fluid confined between **two** of those structureless walls in the microcanonical ensemble, as illustrated in Fig. 1. Use a LJ-fluid (ϵ_{fluid} and σ_{fluid} are the well depth of the potential and the van der Waals radius, respectively) containing $N = 6 \times 6 \times 12$ atoms included in a simulation box of volume V with dimensions $L \times L \times 2L$ along the x, y, and z directions such that the number density is $\rho = N/V = 0.25\sigma_{\text{fluid}}^{-3}$. The walls, located at $z_{w,1}$ and $z_{w,2}$ (in distance $2L$), act on the LJ fluid along the direction normal to the walls, z, through $U_{\text{wall}}(z - z_{w,1})$ and $U_{\text{wall}}(z_{w,2} - z)$, respectively. Use PBC in $x - y$ directions.

$$F_w = \frac{3\sqrt{3}}{2}\epsilon_w\left[-9\frac{\sigma_w^9}{z_f^{10}} + 3\frac{\sigma_w^3}{z_f^4}\right]$$

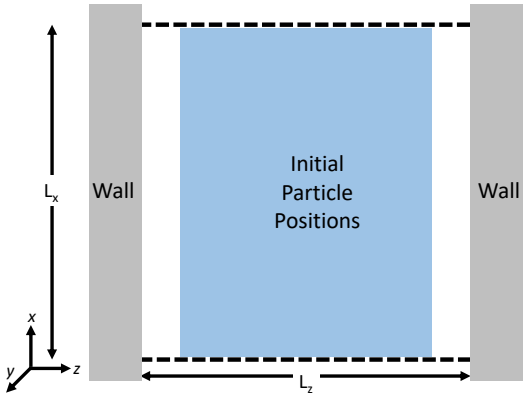

Abbildung 1: Schematic representation of a simulation box with two walls (gray), where the initial particle positions are constrained to the area in blue.

a) Enrich the 3D MD implementation of Exercise sheet #3 with a function that includes the solid-liquid interactions acting on the LJ fluid. Test your implementation with $\epsilon_{\text{fluid}} = 0.1488$ kcal/mol, $\epsilon_{\text{wall}} = 1.4887$ kcal/mol, $\sigma_{\text{fluid}} = 0.188$ nm, $\sigma_{\text{wall}} = 0.0376$ nm, and $T_0 = 300K$. The equilibration and production runs of the confined fluid are performed during 0.1 ns and 0.2 ns, respectively. Provide a representative ovito-snapshot obtained at the end of the production run. During the production run, save the atoms' locations in a trajectory file every 10 time steps. *Hint: Although the proposed duration for the equilibration and production runs required 5 minutes of computational time when testing the sheet, feel free to adjust the duration of the equilibration and production runs according to the performance of your implementation in such a way that the computational time remains reasonable.*

   The density profile in one cartesian dimension, $\rho(z)$, as a function of the position along the direction normal to the walls, z, is formally defined as $\rho(z) = \langle \sum_i \delta(z_i - z) \rangle$, where δ is the Dirac delta-function, and the sum index, i, runs over all the atoms. The $\langle ... \rangle$ average has to be interpreted as time average in your simulation. Similarly, one can define the density profiles in the directions parallel to the walls, $\rho(x)$ and $\rho(y)$. (Calculate and average by histogramming and normalizing as discussed in the lecture and as done, in principle, already for the $g(r)$.)

   Calculate and plot the density profiles along x, y, and z. Comment on your results. Calculate and report the pressure on the two walls exerted by the fluid. The pressure is defined as $\langle \sum_i F_{w,i}(z) \rangle / S_w$ where $F_{w,i}$ is the force exerted on the wall by the particle i on the the wall's surface with area S_w. The average $< .. >$ also includes the average over all particles. What would happen if the walls were not fixed but could freely move? (10 points)

b) Decompose the trajectory of the production run obtained in (a) in 6 blocks of equal time, and calculate for each block the adsorption Γ defined as $\Gamma = \int_{z_{w,1}}^{(z_{w,1}+z_{w,2})/2} (\rho(z) - \rho_b) dz$ where ρ_b is the bulk density, i.e. the density defined at the box center $z = (z_{w,1} + z_{w,2})/2$. Calculate and report the corresponding statistical error for Γ. (4 points)

c) Perform similar simulations as in (a) but now with $\epsilon_{\text{fluid}} = 0.25 k_B T_0$ and $\epsilon_{\text{wall}} = 0.1 k_B T_0$, $\epsilon_{\text{wall}} = 0.25 k_B T_0$ and $\epsilon_{\text{wall}} = k_B T_0$. Provide representative ovito-snapshots obtained during the production run for each value of ϵ_{wall}. Plot in the same plot the density profile, $\rho(z)$ versus z for the three values of ϵ_{wall}. Interpret your results. (4 points)

d) Perform similar simulations as in (a), but now with applying an external constant force, $F^{app} = k \epsilon_{\text{fluid}} / \sigma_{\text{fluid}}$ with $k \in (1, 10, 100)$, on each atom of the LJ fluid along the z-direction. The equilibration and production runs are 10^4 time steps, respectively. Provide

an ovito-snapshot at the end of each production run. Interpret your ovito-snapshot. If you have time and fun, compare to the barometric height law $\rho(z) \propto \exp(-\beta F^{app}\, z)$ which you obtain if you switch off the particle-particle LJ interaction, i.e., you simulate an ideal gas. Note that all profiles have to be normalized properly to compare, i.e., $\int_0^{L_z} dz \rho(z) = N/S_w$. (2 points + 2 extra points for the comparison with the barometric height law)

Numerical values of quantities to be used:

quantity	value (units)
k_B	0.0019849421 (kcal/mol/K)
ϵ_{fluid}	0.297741315 (kcal/mol) or text
σ_{fluid}	0.188 (nm)
T_0	300 (K)
mass	39.95 (g/mol)
Δt	2 (fs)
t_{eq}	0.1 (ns)
t_{prod}	0.2 (ns)