

Exercise 4 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 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, $z_{\text{max}} = 2.5\sigma_{\text{wall}}$** , 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.

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

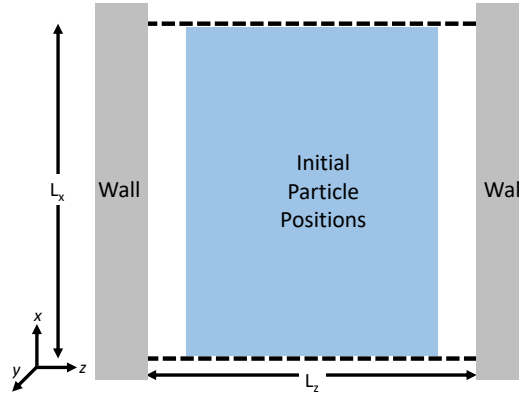


Abbildung 1: Schematic representation of a simulation box with two walls (gray), where the initial particle positions are constrained to the area in blue.

- 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 $\epsilon_{\text{fluid}} = 0.1488 \text{ kcal/mol}$, $\epsilon_{\text{wall}} = 1.4887 \text{ kcal/mol}$, $\sigma_{\text{fluid}} = 0.188 \text{ nm}$, $\sigma_{\text{wall}} = 0.0376 \text{ nm}$, and $T_0 = 300 \text{ K}$. 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 $\langle \dots \rangle$ 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 $\langle \dots \rangle$ 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 $\epsilon_{\text{fluid}} = 0.25k_B T_0$ and $\epsilon_{\text{wall}} = 0.1k_B T_0$, $\epsilon_{\text{wall}} = 0.25k_B T_0$ 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, $F^{\text{app}} = k\epsilon_{\text{fluid}}/\sigma_{\text{fluid}}$ 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) |

