

MD/GE - Molecular dynamics simulation and lattice energy of argon

Protocol for the PC 2 lab course by
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Abstract:

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1 Theory

Molecular dynamics simulations (MDS) are used to visualize spatial movements of atoms and molecules. For that a numerical algorithm can determine the positions r_i and momentums p_i for each particle i .^[1] A proven algorithm is the Velocity-Verlet algorithm, which assigns each particle a random starting position and velocity at first before calculating the new positions and velocities a small time step later. That is achieved by calculating the new accelerations using the provided potential, e.g. Lennard-Jones potential. So for the computation of particle trajectories in MDS the equation of motion is integrated and then the forces induced by potentials are calculated. To approximate the intermolecular interactions between particles, the Lennard-Jones potential (LJ-potential) V_{ij} with equation 1 is used.^[1]

$$V(r_{ij}) = 4\varepsilon_0 \left[\left(\frac{\sigma_0}{r_{ij}} \right)^{12} - \left(\frac{\sigma_0}{r_{ij}} \right)^6 \right], \quad (1)$$

σ_0 describes the minimum distance, r_{ij} the distance between particle i and j and ε_0 the depth of the potential well at the equilibrium distance r_e , which can be seen in figure 1. The positive part with a twelfth power-term characterizes the repulsive interactions to the nearest neighbours, whereas the negative part with a sixth power-term characterizes the attractive electrostatic interactions.^[1]



Figure 1: Potential curve of a Lennard-Jones potential V_{ij} depending on the particle distance r_{ij} .^[1]

In MDS reduced properties are used to describe thermodynamical states by defining units and setting the value to 1.0 for shorter calculation times. When using the LJ-potential the fundamental units ε_0 , σ_0 and the mass m are set to 1.0. In the experiment the reduced units of pressure p^* and temperature T^* are used, which can be calculated with equation 2 and 3.

$$T^* = \frac{k_B T}{\varepsilon_0} \quad (2)$$

$$p^* = \frac{p \sigma_0^3}{\varepsilon_0} \quad (3)$$

In an isolated system, where the gaseous and solid phase are in equilibrium and the volume of the gas is much bigger than the volume of the liquid, the Clausius-Clapeyron equation 4 can be used to describe the dependence of the sublimation pressure p on the temperature T .

$$\ln p = -\frac{\Delta H_{\text{sub}}}{RT} + C \quad (4)$$

The enthalpy of sublimation ΔH_{sub} can be determined by plotting $\ln p$ against $1/T$. Argon behaves like an ideal gas at 70 K and the internal energy ΔU during a phase transition from solid to gaseous is the difference of the corresponding internal energies. Because the translational energy of gaseous argon corresponds to the kinetic theory of gases, the total internal energy of the solid U_s can be calculated with equation 6.

$$U_s = \frac{5}{2}RT - \Delta H \quad (5)$$

U_s consists of two parts, which are described in equation 5.^[1]

$$\Delta U_s = U_{\text{lattice}} + U_{\text{vib}} \quad (6)$$

The first part corresponds with the potential energy of argon atoms at rest on their lattice planes, whereas the second part is the vibrational energy of the atoms. For the calculation of U_{vib} , Debye's theory is used, which states that the crystal is composed as independent vibrating lattice atoms with varying frequencies. For that the equation 7 shows the connection between the vibrational energy and the Debye-temperature Θ_D .

$$U_{\text{vib}} = \frac{9}{8}R\Theta_D + 3RTD\left(\frac{\Theta_D}{T}\right) \quad (7)$$

To calculate the theoretical value of the lattice energy, equation 8 can be used, which is derived from the pair potentials $V_{ij}(r_{ij})$ in the LJ-potential equation 1.

$$U_{\text{lattice}}(s) = 2N_A\varepsilon_0 \left[12.132 \left(\frac{\sigma_0}{a} \right)^{12} - 14.454 \left(\frac{\sigma_0}{a} \right)^6 \right] \quad (8)$$

N_A is Avogadro's constant and a the distance between atoms. For Argon the best values, which were determined from other properties of the gas, are $\varepsilon_0 = 1.643 \times 10^{-21}$ J and $\sigma_0 = 3.41 \times 10^{-10}$ m.^[2]

2 Procedure

2.1 Molecular Dynamics Simulations

2.2 Lattice Energy of Argon

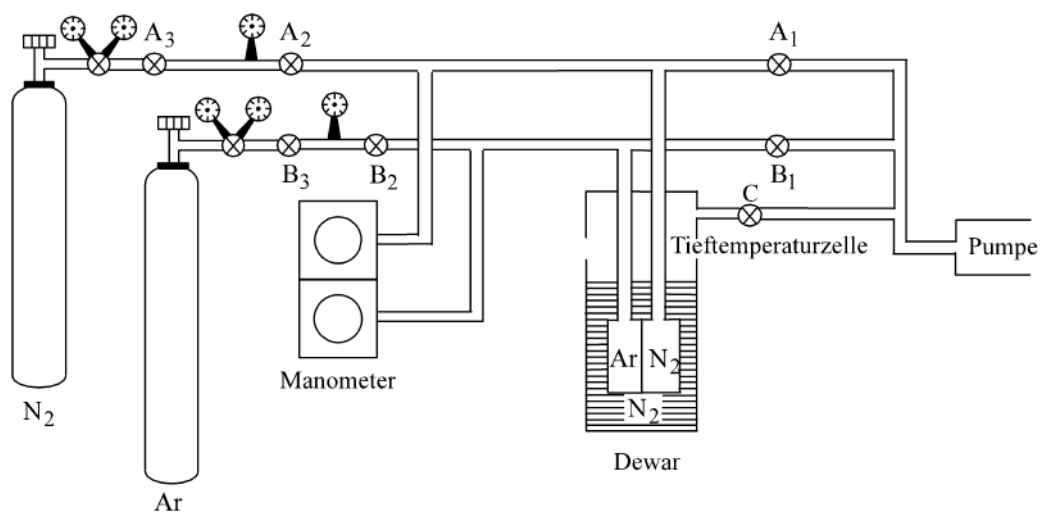


Figure 2: Scheme of the measuring apparatus.^[1]

3 Results

$$\log(p/\text{Torr}) = 7.781845 - \frac{341.619 \text{ K}}{T} - 0.0062649 \frac{T}{\text{K}} \quad (9)$$

4 Analysis

4.1 Molecular Dynamics Simulations

4.1.1 Isochor simulations

The temperatures and pressures calculated in the simulations of the second task are reported in reduced units and shown in Figure 3.

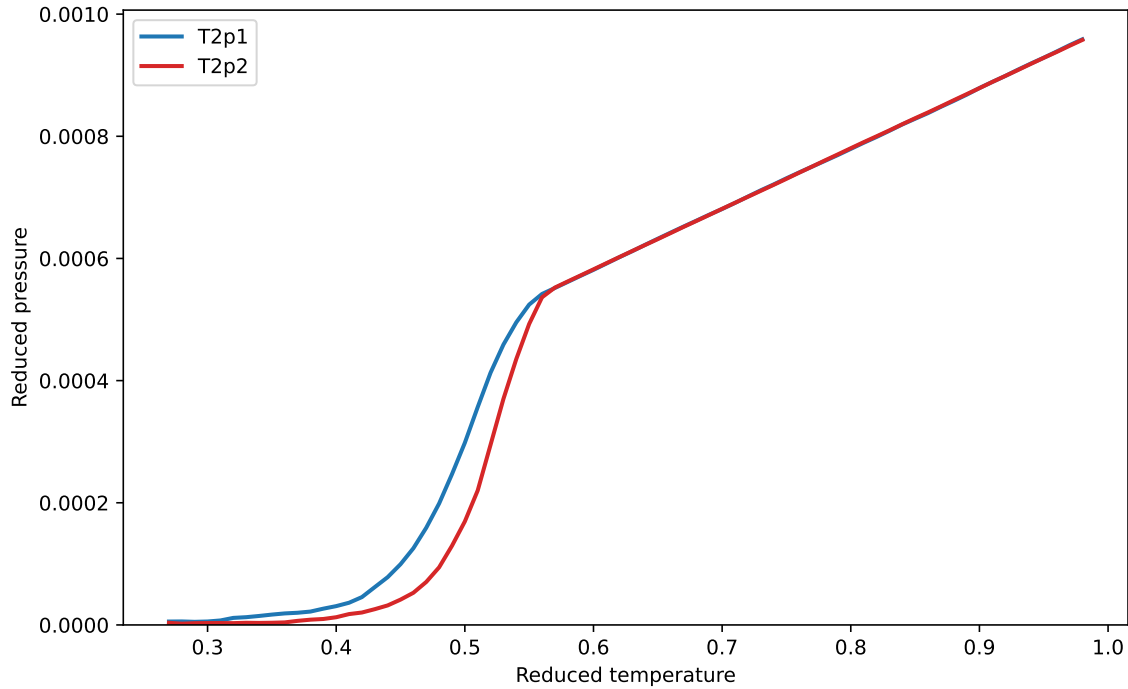


Figure 3: The reduced temperature is plotted against the reduced pressure for 100 cycles and 1000 steps (T2p1, blue) and for 200 cycles and 4000 steps (T2p2, red).

Both simulations show a very low incline before the sublimation, a steep slope while the sublimation and a transition into a linear increase of the pressure after the sublimation has ended. By increasing the number of iteration steps and the number of iterations per temperature from the first simulation T2p1 to the second T2p2, the begin of the big increase in pressure shifts to a higher temperature, while both curves lead to the same value of pressure, from which on they show the same linear increase. To compare the simulation results to the experimental results, the values of the reduced temperature and pressure are converted from reduced units into Kelvin and Pascal by using equations 2 and 3. The new values are then plotted with the experimental data from ??, which is shown Figure 4.

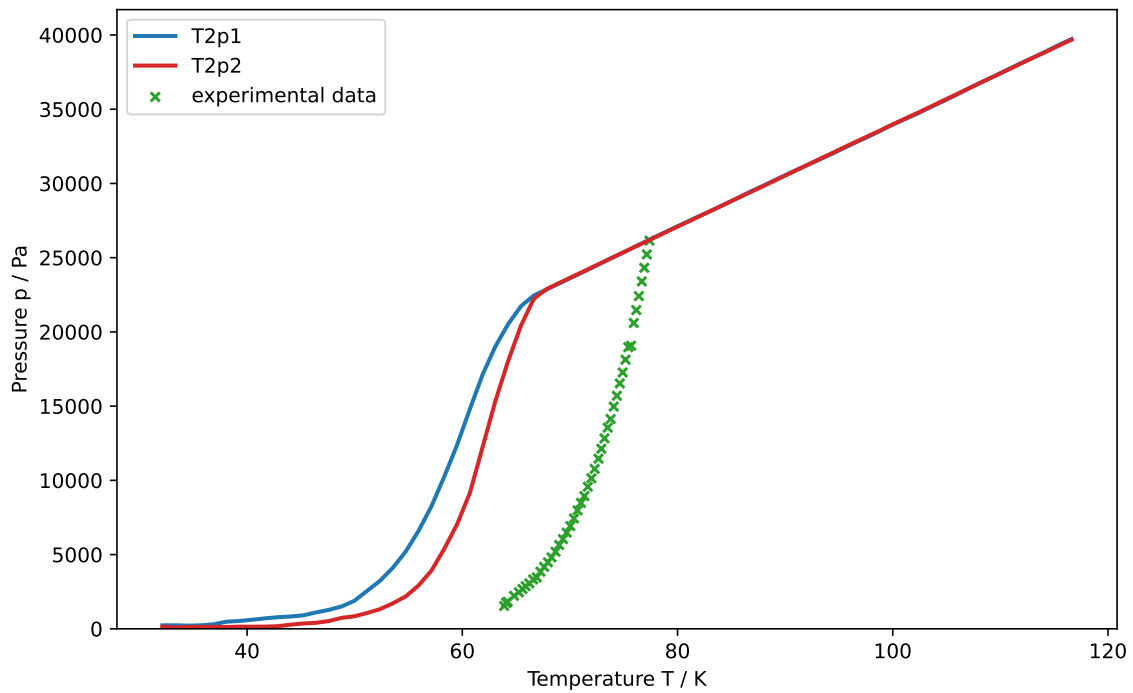


Figure 4: The converted temperature is plotted against the converted pressure from the short simulation (T2p1, blue), long simulation (T2p2, red) and the experimental values (green).

Figure 4 shows that the sublimation curve of the longer simulation with more iteration steps and cycles is closer to the experimental data than the shorter simulation. But still, the experimental sublimation curve is located around 10K higher, which can be caused by the approximation of the interactions, which are made in the Lennard-Jones potential. Furthermore, it can be concluded that a higher computation time with more iteration steps and cycles in the Velocity-Verlet algorithm would be necessary to fit the simulation values to the experimental values.

4.1.2 Isobaric simulations

4.2 Lattice Energy of Argon

5 Error Discussion

6 Conclusion

7 References

- [1] H. Dilger, *2025-pc2-script-en*, **2025**.
- [2] J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, *The molecular theory of gases and liquids*, John Wiley & Sons, **1964**.