

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]

$$V(r_{ij}) = 4\epsilon_0 \left[\left(\frac{\sigma_0}{r_{ij}} \right)^{12} - \left(\frac{\sigma_0}{r_{ij}} \right)^6 \right], \quad (1)$$

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]

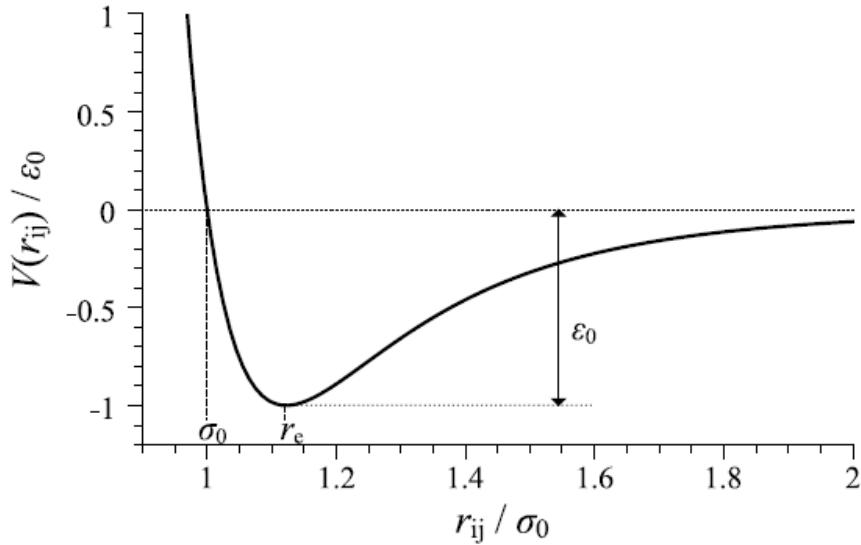


Figure 1: Potential curve of a Lennard-Jones potential V_{ij} depending on the particle distance r_{ij} .^[1]

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} , Debyes 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

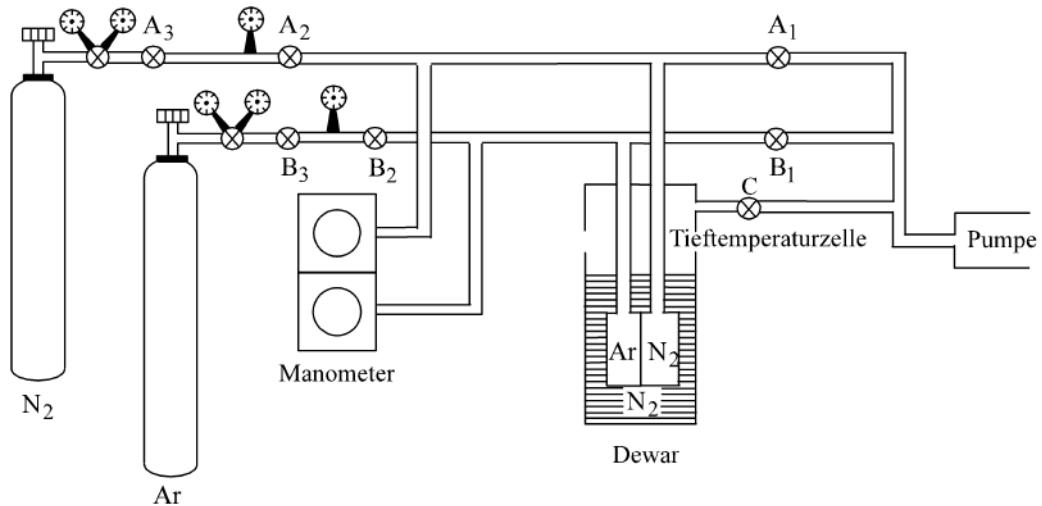


Figure 2: Scheme of the measuring apparatus.^[1]

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 Visualization of the particle movement

4.1.2 Isochor sublimation of argon

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

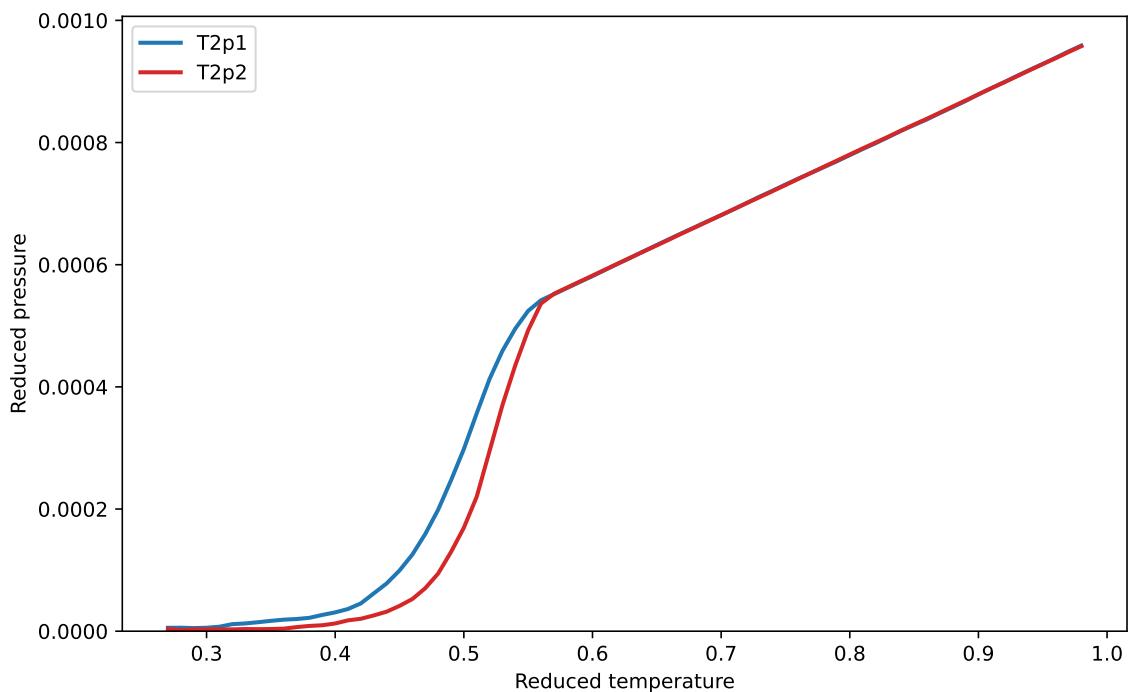


Figure 3:

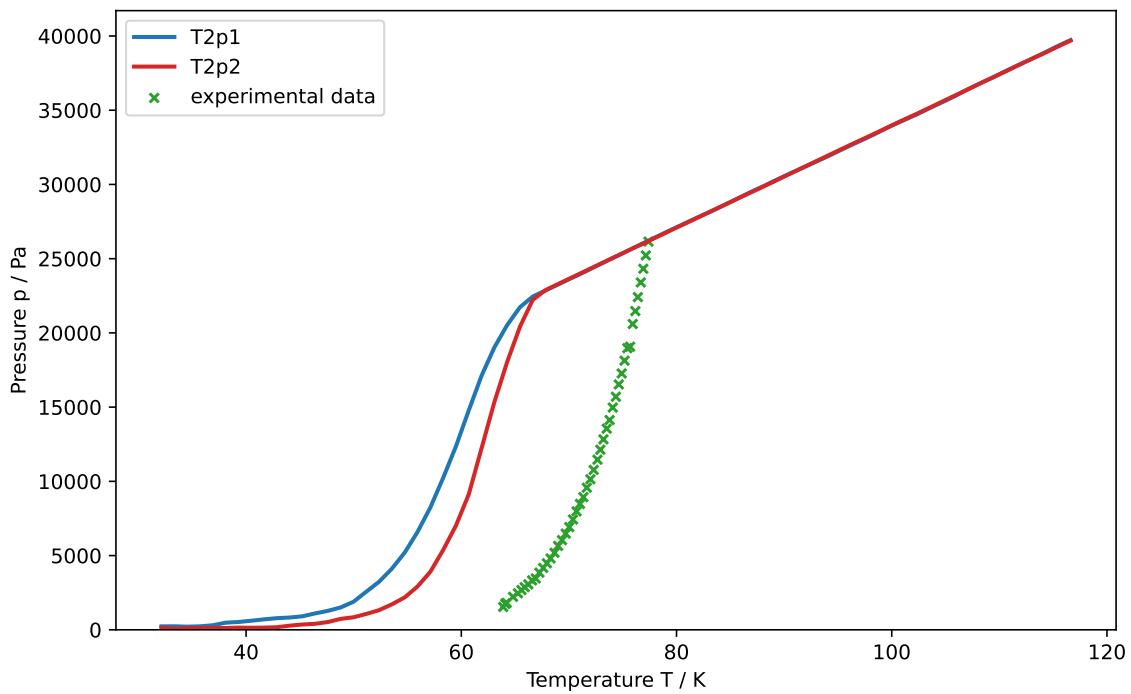


Figure 4:

4.1.3 Isobar sublimation of argon

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.