2D Clausius–Clapeyron equation

Aim:

Verify the Clausius–Clapeyron equation by simulations of a 2D model of matter

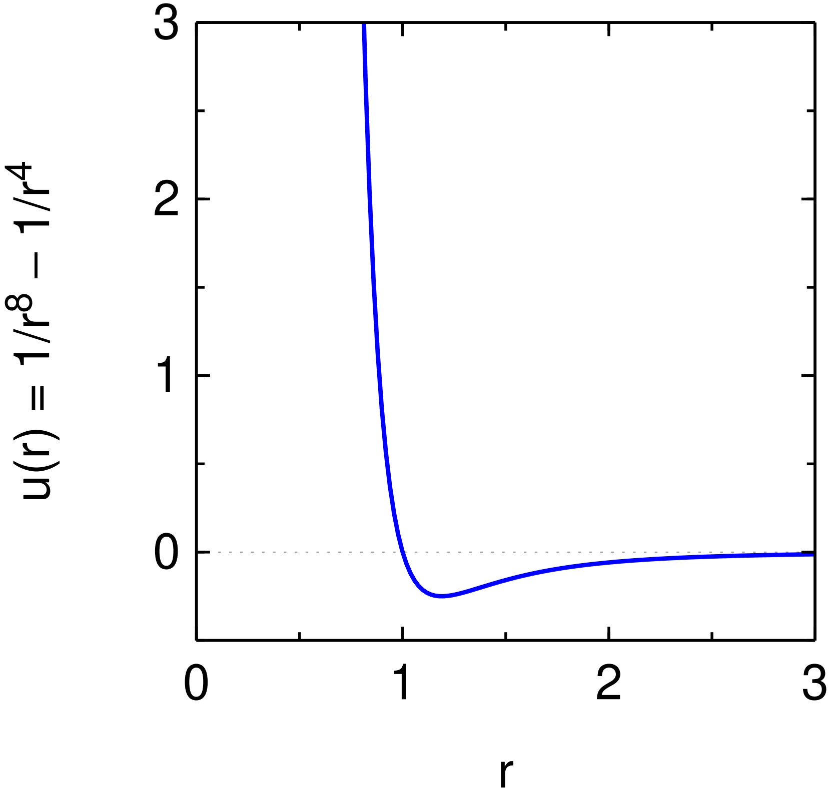
Model:

8-4 type potential (≈ Lennard-Jones in 2D)

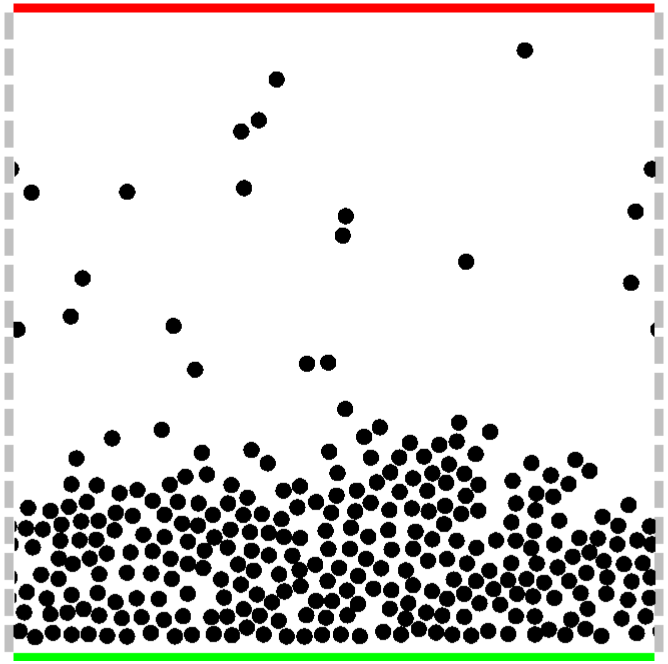
$$u(r) = \frac{1}{r^8} - \frac{1}{r^4}$$

Hard attractive (7-3) or repulsive (r^{-7}) walls.

- Reduced units: $k_B = R/N_A = 1$, energy and temperature are measured in the same units
- Quantities given per 1 atom, not per 1 mol (subscript $_{at}$)



Tasks



- In a system of two phases separated by a flat interface, determine the equilibrium vapor pressure in dependence on temperature (at least two points). Use MD with a thermostat.
- Calculate the mean temperature and pressure, then simulate the vapor in MC and determine the compressibility factor.
- Calculate the vaporization enthalpy from the Clausius–Clapeyron equation (corrected to non-ideal behavior of vapor), including the estimated standard error.
- Determine the vaporization enthalpy from the averaged potential energy of liquid in the periodic boundary contitions.
- Compare both values.

Simulation methods

- The simulation starts from a random configuration using MC (to remove overlaps), then it automatically switches to MD.
- Method: leap-frog + Berendsen thermostat[*]
- Monte Carlo (Metropolis) is possible, too (for some subtasks)
- **Pressure = averaged force on the top wall**:

$$p^{\text{wall}} = \left\langle \frac{f_{\text{wall}}}{L} \right\rangle, \quad L = \text{edge length}$$

$\langle\cdot\rangle$ = averaging of instantaneous values during the simulation

- Alternatively, **pressure from the virial of force** (no wall needed):

$$p_{yy} = \rho k_{\mathrm{B}} T + \frac{1}{DV} \left\langle \sum_{\text{all forces}} r_y f_y \right\rangle$$

p_{yy} = diagonal component of the pressure tensor in the direction of $\hat{y}$,
$\rho = N/V$ = number density[†], $V = L^D$, L = edge length, D = dimension ($D = 2$), the sum is over all pair forces (particle–particle, wall-particle)

[*] other types can be used, too

[†] sometimes denoted $\mathcal{N}$ or n

Vaporization enthalpy from the Clausius–Clapeyron equation

The Clausius–Clapeyron equation

$$\Delta_{\mathrm{vap}}H_{\mathrm{m}} = -\frac{R\ln(p_1/p_2)}{1/T_1 - 1/T_2}$$

is derived using the following simplifications:

- The vaporization enthalpy does not depend on temperature
- Liquid volume ≪ vapor volume
- The ideal gas equation of state holds for the vapor phase.

In the simulation, the first two simplifications are valid (error < 2%), however, non-ideality is important (error ≈ 15%). We will assume instead:

- The compressibility factor of gas, $Z = p/\rho k_{\mathrm{B}}T$, at the saturated vapor pressure does not depend on temperature.

The corrected Clausius–Clapeyron equation is:

$$\Delta_{\mathrm{vap}}H_{\mathrm{at}} = -Z\frac{\ln(p_1/p_2)}{1/T_1 - 1/T_2}$$

where Z is approximated by the value at $T = (T_1 + T_2)/2$

Vaporization enthalpy from the mean potential energy

From the known formula $H = U + pV$ we get

$$\Delta_{\text{vap}} H_{\text{at}} = \Delta_{\text{vap}} U_{\text{at}} + p \Delta_{\text{vap}} V_{\text{at}} = \left\langle \frac{E_{\text{pot}}(\text{g}) - E_{\text{pot}}(\text{l})}{N} \right\rangle + \frac{p}{\rho(\text{g})} - \frac{p}{\rho(\text{l})}$$

where $\rho = N/V$ = number density

Crude approximation

- $\rho(\text{l}) \gg \rho(\text{g})$
- $E_{\text{pot}}(\text{g}) \approx 0$
- vapor = ideal gas

$$\Delta_{\text{vap}} H_{\text{at}} \approx -\left\langle \frac{E_{\text{pot}}(\text{l})}{N} \right\rangle + k_{\text{B}} T$$

Better approximation

- $\rho(\text{l}) \gg \rho(\text{g})$

$$\Delta_{\text{vap}} H_{\text{at}} \approx \left\langle \frac{E_{\text{pot}}(\text{g}) - E_{\text{pot}}(\text{l})}{N} \right\rangle + Z k_{\text{B}} T$$

SIMOLANT – installation (Windows)

- http://www.vscht.cz/fch/software/simolant
  or Google simolant
- Download `simolant-win32.zip`
- Create a folder and unpack SIMOLANT there.
  Do not run directly from `simolant-win32.zip`!
- Run `simolant.exe`

Hint: The calculated data are exported to file `simolant.txt` with a decimal point. If you like decimal comma (useful with Czech localization), click ▮, in panel “Measure”.

Hint: If you restart SIMOLANT, the old `simolant.txt` is renamed to `simolant.bak`. The export name `simolant` can be changed by Menu: File → Protocol name..

Vapor pressure – setup

- Default number of atoms = 300. On a slow computer, decrease the number of atoms (slider “N”), but not below 150.
- Menu: Prepare system → Vapor-liquid equilibrium
- Menu: Show → Quantities
- Slider “simulation speed” (right bottom) to maximum (only every 15th configuration is shown and analyzed)
- Slider “measurement block” to maximum (block = average of 100 points)

Hint: some speed can be gained by turning off drawing using selector: draw mode: Nothing

Vapor pressure – simulation at T_1

- Set temperature (leftmost slider “T”, not “τ”) to $T_1 \in [0.15, 0.16]$
  - the value of “T” is shown in the data block top right
  - the lower temperature, the more precise ... but a faster computer is needed
  - **Hint:** fine slider move = cursor keys ↑ and ↓
  - **Hint:** also can be typed to field cmd: `T=0.155` + Enter
- Simulate until the system is equilibrated
- Click ▮record. Do not change simulation parameters during recording!
- After a while, click ▮record again. Results will be shown. The recommended number of blocks is > 50, better > 100, a relative error in P(top wall)[‡] should be less than 10 %.
  - If not reached, select continue.
  - If OK, save the results using button save (overwrite... .

[‡] you can try also Pyy

Vapor pressure – simulation at T_2

- Repeat for a higher temperature $T_2 \in (0.19, 0.20)$
  - a smaller number of blocks (25–50) is sufficient because the pressure is higher and the statistical error smaller (but the gas is less ideal)
- Record the results by ▮record; since file `simolant.txt` is present, you will be prompted by append to simolant.txt and clear

Data analysis I

The results are in file `simolant.txt`.

If you executed several times append to..., you will find several data blocks.

- In block “Measurement #1”, find temperature Tkin and pressure P (top wall), denote them as p_1 and T_1.
  - Tkin differs slightly from the temperature set because of finite-size and thermostat errors
  - alternatively, Pyy can be used as p_1
- Find the value p_2 for temperature T_2 from block “Measurement #2”
- Calculate the mean temperature and pressure:

$$\overline{T} = \frac{T_1 + T_2}{2}, \quad \overline{p} = \sqrt{p_1 p_2}$$

- Calculate the “mean number density” of vapor using the ideal gas equation of state:

$$\overline{\rho} = \overline{p}/\overline{T}$$

Compressibility factor (Monte Carlo)

of gas will be calculated in the periodic boundary contitions.

- Menu: Show → Quantities . . . already set
- Menu: Boundary conditions → Periodic
- Menu: Method → Monte Carlo (Metropolis)
- Set temperature to $\overline{T} = (T_1 + T_2)/2$ using cmd: T=*number* + Enter
- Set the the density to $\overline{\rho} = \overline{p}/\overline{T}$: rho=*number* + Enter
- Equilibrate
- Click ▮record, simulate for at least 10 blocks; save the results
- Re-open `simolant.txt` and find the last value of Z
- In addition, find Epot (will be used later as $E_{\text{pot}}(\text{g})$)
- For a higher precision, re-set density to $\rho = \overline{p}/Z$ and repeat the simulation (then the final p will be closer to $\overline{p}$)

The standard approach is the NPT ensemble for $p = \overline{p}$, which is not (for several reasons) implemented in SIMOLANT.

If you get bored... MC or MD? +

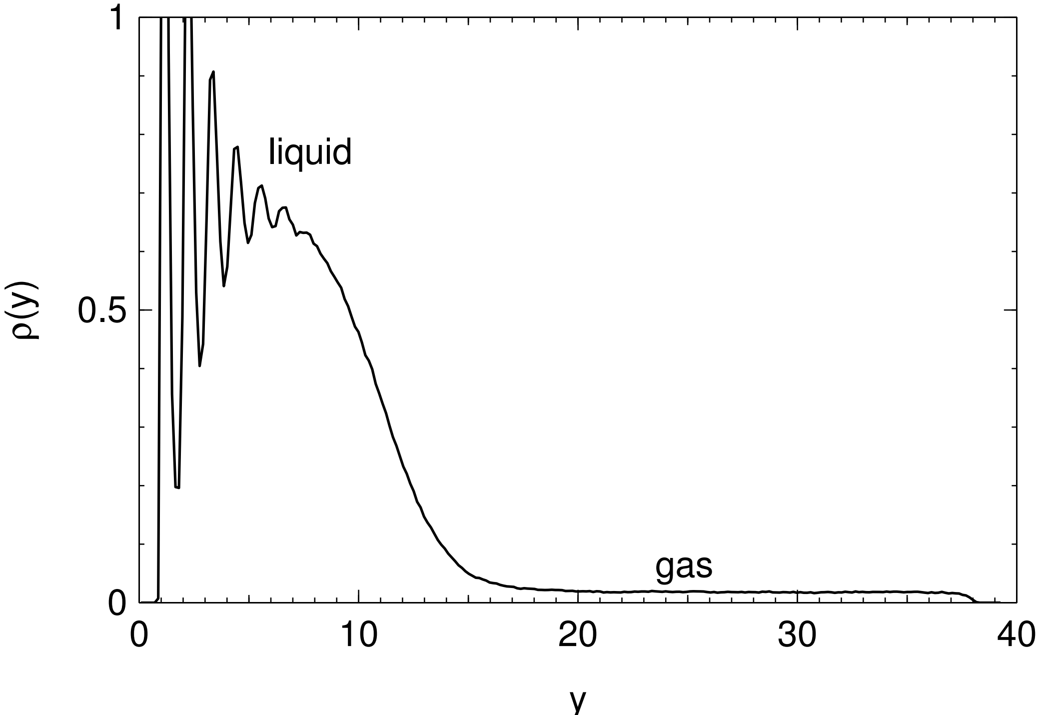
- Repeat the previous calculation with

  Menu: Method → MC→MD (Berendsen)
- Compare both methods. Which method is more accurate? Why?

If you get bored... another method for Z +

It is possible to determine the vapor density in the equilibrium slab simulation:

- Menu: Show → Vertical density profile
- In `simolant.txt` you will find the density profile. Plot it (e.g., after importing to Excel) and determine the gas density ρ_1, then $Z_1 = p_1/\rho_1$. Repeat for T_2.
- Make an average of both Zs.



Vaporization enthalpy from the saturated pressures

- Calculate from the values obtained above (where $k_\mathrm{B} = 1$):

$$\Delta_\mathrm{vap} H_\mathrm{at} = -Z \frac{\ln(p_1/p_2)}{1/T_1 - 1/T_2}$$

- Do not forget to estimate the statistical (random) errors (uncertainties)! In the results, the standard errors[§] estimated using the block method are given.
  It is sufficient to consider the errors in p_1 and p_2, because the temperatures and Z are much more precise.

$$\delta(\Delta_\mathrm{vap} H_\mathrm{at}) = Z \frac{\sqrt{\delta_\mathrm{rel}(p_1)^2 + \delta_\mathrm{rel}(p_2)^2}}{|1/T_1 - 1/T_2|}$$

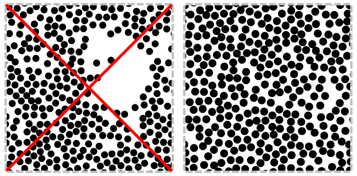
[§] Standard error = estimated standard deviation of the average caused by stochastic noise. *Uncertainty* includes both the stochastic and systematic errors.

Vaporization enthalpy from the internal energy

- Menu: Boundary conditions → Periodic
- Menu: Show → Quantities

$\Big\}$ already set

- Set temperature to $T=(T_1+T_2)/2$
- Both MC and MD are appropriate.
- To speed up, you may decrease “measurement block” a bit
- Slide “ρ” (density) until pressure (blue P=... in the panel) fluctuates around zero (precisely around $p=\sqrt{p_1 p_2}$). The configuration must be a homogeneous liquid without cavities.



Hint: cursor keys ↑ ↓ in the slider

- Put down the value of Epot = $\langle E_\text{pot}(\text{l})\rangle$ (the error is small).
- $E_\text{pot}(\text{g})$ comes from slide 11.
- Calculate: $\Delta_\text{vap}H_\text{at}=\left\langle\dfrac{E_\text{pot}(\text{g})-E_\text{pot}(\text{l})}{N}\right\rangle+ZT$
- Less accurate version for ideal vapor: $\Delta_\text{vap}H_\text{at}=-\left\langle\dfrac{E_\text{pot}}{N}\right\rangle+T$
- Compare with the Clausius–Clapeyron-based result.