Verification of the Clausius–Clapeyron equation

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

Software: SIMOLANT

Model: 8-4 type potential (≈ Lennard-Jones in 2D)
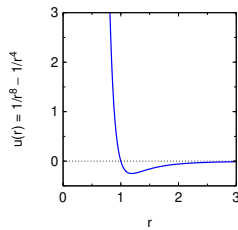
$$u(r) = \frac{1}{r^8} - \frac{1}{r^4}$$

truncated at $r_c = 4$ and smoothly sewed in.

Attractive walls = potential u integrated over a continuous distribution of particles with number density $\rho = N/V = 0.75$:

$$u_{\text{wall}}(d) = \rho\pi\left(\frac{5}{24d^6} - \frac{1}{d^2}\right)$$

Repulsive walls do not contain $-\frac{1}{d^2}$

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: simulations #1, #2). Use MD with a thermostat.
- Calculate the mean temperature and pressure, then simulate the vapor by MC and determine the compressibility factor (simulation #3).
- Calculate the vaporization enthalpy from the Clausius–Clapeyron equation (corrected for non-ideal behavior of vapor), including the estimated standard error.
- Determine the vaporization enthalpy from an *NPT* simulation of liquid (simulation #4) and vapor (simulation #3) in the periodic boundary contitions.
- Compare both values.
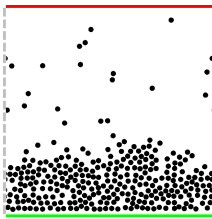
Simulation methods

- The simulation starts from a random configuration using MC (to remove overlaps), then it automatically switches to MD.
- Recommended method for the equilibrium: Bussi or Berendsen thermostat; other methods incl. MC are possible, too.
- Recommended method for gas and liquid separately: *NPT* MC (*NPT* MD is also possible).
- **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):

$$p_{yy} = \rho k_B T + \frac{1}{DV}\left\langle\sum r_y f_y\right\rangle$$

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).

*sometimes denoted $\mathcal{N}$ or n

Vaporization enthalpy from the Clausius–Clapeyron equation

The Clausius–Clapeyron equation (NB: per atom and in our units $R \equiv 1$)

$$\Delta_{\text{vap}}H_m = -\frac{R\ln(p_1/p_2)}{1/T_1 - 1/T_2}$$

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 (± 2%), however, nonideality is sizeable (≈ 30% for T=0.75). More accurate approximation:

- The compressibility factor of gas at the saturated vapor pressure does not depend on temperature.

The corrected Clausius–Clapeyron equation is: ($k_B \equiv 1$)

$$\Delta_{\text{vap}}H_{at} \approx -Zk_B\frac{\ln(p_1/p_2)}{1/T_1 - 1/T_2}$$

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

Compressibility factor:

$$Z = \frac{pV}{nRT} = \frac{p}{\rho k_B T}$$

Vaporization enthalpy from *NPT* simulations of liquid and gas

A simulation at constant temperature and pressure (*NPT* ensemble: N = constant number of particles, P = constant pressure, T = constant temperature) gives the enthalpy:

$$H = \langle E_{\text{pot}}\rangle + \langle E_{\text{kin}}\rangle + P\langle V\rangle$$

In order to get the vaporization enthalpy, both vapor and liquid is simulated:

$$\Delta_{\text{vap}}H_{at} = \frac{H(g) - H(l)}{N}$$

Also, Z of vapor for the last step is determined

NB. In 3D, vapors are dilute and the following approximations hold:

- $\rho(l) \gg \rho(g)$ ($\rho = N/V$ = number density)
- vapor = ideal gas $\Rightarrow p\langle V\rangle \approx k_B T$
- $E_{\text{pot}}(g) = 0$ for molecules without internal degrees of freedom (e.g., vibrations)

In addition, $\langle E_{\text{kin}}(g)\rangle = \langle E_{\text{kin}}(l)\rangle = \frac{f}{2}k_B T$. Therefore, gas simulation is not needed:

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

i.e., one simple *NVT* simulation suffices.

SIMOLANT – installation (Windows)

- http://old.vscht.cz/fch/software/simolant
  or Google simolant
- Download `simolant-win32.zip`
- Unpack to a suitable folder.
  Do not run directly from `simolant-win32.zip`, you would not find files. . .
- Run `simolant.exe`

Hints:

- 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". SIMOLANT does not detect the localization.
- If you restart SIMOLANT, the old `simolant.txt` is renamed to `simolant.bak`. Optionally, 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
  or Energy/enthalpy convergence profile[a]
- 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:
draw mode: Nothing
Do not forget to return back to know what's going on!

[a]But not Minimum – nothing would be calculated!
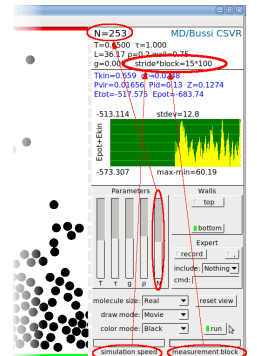
Vapor pressure – simulation #1 at T_1

- Set temperature (leftmost slider "T", not "τ") to $T_1 \in [0.5, 0.6]$
  – the value of "T" is shown in the data block top right
  – the lower temperature, the more precise . . . but a faster computer is needed
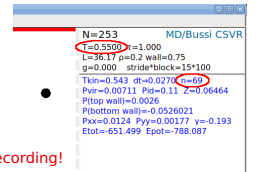 - geeks with cool comps: use $T_1 = 0.5$
  - school notebooks: use $T_1 = 0.6$
  - golden mean: use $T_1 = 0.55$
  – **Hint:** fine slider move = cursor keys ↑ and ↓
  – **Hint:** also can be typed to field cmd: T=0.55 + Enter
- Simulate until the system is equilibrated
- Click ▌record . Do not change simulation parameters during recording!
- After a while, click ▌record again. The results will be shown. The recommended number of blocks (n= right top) is at least 50, better over 100. The relative standard error of quantity P(top wall)[†], as given in (), should be less than 10%.
  – If not accurate enough, select continue .
  – If OK, select save (overwrite "simolant.txt" and clear) .

[†] optionally Pyy

Vapor pressure – simulation #2 at T_2

- Repeat for a higher temperature, approximately $T_2 = T_1 + 0.15 \in [0.65, 0.75]$
  A smaller number of blocks (about one half as for T_1) is sufficient because the pressure is higher and the relative statistical error smaller (but the gas is less ideal)
- Record the results by ▌record ; since file `simolant.txt` is present, you will be prompted append to "simolant.txt" and clear

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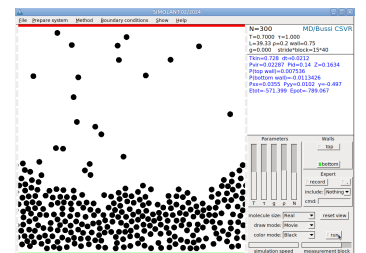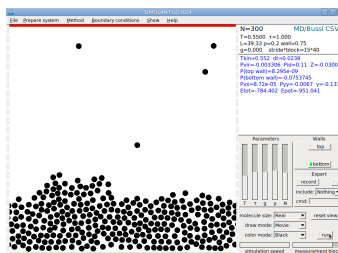
Data analysis I

The results are in file `simolant.txt`.

You should find two data blocks headed with lines:
```
========== MEASUREMENT ========== # 1 ==========
========== MEASUREMENT ========== # 2 ==========
```
If you have typed append to... more than twice, you will find more blocks...

- In block #1, find temperature Tkin and pressure P (top wall), denote them as p_1 and T_1.
  – Tkin may only slightly differ from the temperature T_1 you have set.
  – Alternatively, the virial pressure component Pyy can be used as p_1.
    It should be on average the same, but it is a bit less accurate (more statistical noise).
- Find the value p_2 for temperature T_2 from block #2
- Calculate the mean temperature and pressure:

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

Note the geometric mean for pressure – the pressure–temperature dependence is exponential.
Be careful, in case of a wrong value, the subsequent simulations would be wrong!

Compressibility factor of gas in the *NPT* ensemble: simulation #3

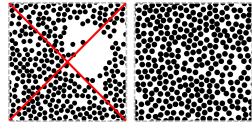will be calculated in the periodic boundary contitions. At low pressure, MC is more efficient.

- Menu: Boundary conditions → Periodic
- Set temperature to $\overline{T} = (T_1 + T_2)/2$ using cmd: T=*number* + Enter
- Set pressure to $\overline{p} = \sqrt{p_1 p_2}$: P=*number* + Enter
- Menu: Method → Monte Carlo *NVT* (Metropolis)
- Slider "ρ" to the lowest value (gas); if a big droplet persist, set in cmd: rho=0.001 + Enter
- Menu: Method → Monte Carlo NPT (Metropolis) . Droplets should disappear!
- Menu: Show → Volume convergence profile and reset view (right bottom)
- Slider "measurement block" can be shortened a bit to gain speed
- Let equilibrate, check that you see gas, and turn ▮set MC move off.
- Push ▮record and generate 10–20 blocks.
- Save using ▮record
- Find the value of Z in the last data block in simolant.txt
- Find also enthalpy H – will be needed later as $H(g)$

In the productive MC run, the displacement sizes must be constant!
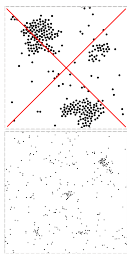
Vaporization enthalpy from *NPT* simulations #3 and #4

Repeat the calculation of page 11 for liquid (simulation #4). You have already set the periodic boundary contitions, temperature, and pressure. Continue:

- Push ▮set MC move to get the trial displacement adjusted
- Menu: Method → Monte Carlo NVT (Metropolis)
- Slide "ρ" (density) until the configuration is a homogeneous liquid without cavities and pressure fluctuates around $\overline{p}$ →
- Menu: Method → Monte Carlo NPT (Metropolis) [§]
- Let equilibrate and turn ▮set MC move off.
- Push ▮record and generate at least 10 blocks
- Save using ▮record
- Find the value of enthalpy H of liquid
- Calculate the vaporization enthalpy $\Delta_{vap}H_{at} = \dfrac{H(g) - H(l)}{N}$ and its standard error

In the productive MC run, the displacement sizes must be constant!

[§]MD NPT Berendsen is also possible, with a slightly higher systematic error

Vaporization enthalpy from the Clausius–Clapeyron equation

- Calculate the vaporization enthalpy from the values obtained above (T_1, p_1 from #1, T_2, p_2 from #2, Z from #3):

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

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

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

where $\sigma_{rel}(p_i)$ are relative errors, in file simolant.txt given in %

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

Results and discussion

- Write down both results of the vaporization enthalpy:
  - from the Clausius–Clapeyron equation, and
  - from the difference of the enthalpies of liquid and gas.
- Are both values in agreement at the 95% confidence level? To answer this question:
  - Calculate the difference of both values,
  - calculate the standard error of this difference,
  - determine the 95% confidence range.
- Which method of determining the vaporization enthalpy is more accurate?
- Which method is subject to more severe systematic errors?
- What is the most common method used in real experiment to determine the vaporization enthalpy?