Simulation study of the Kelvin equation in 2D

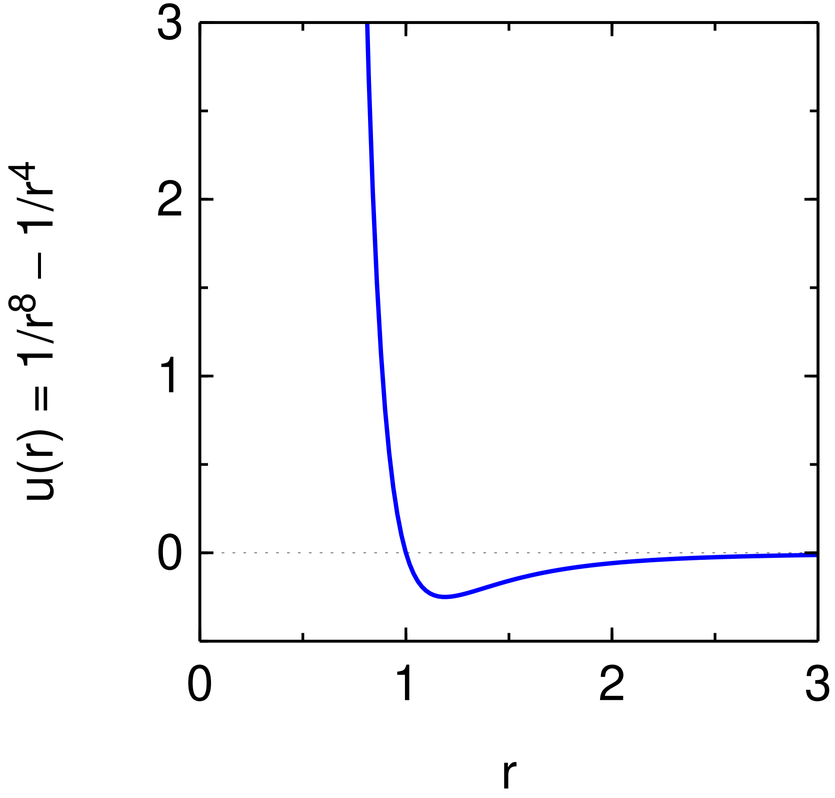
Aim: Verify the Kelvin equation using simulation of a 2D model of matter

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 $\rho = N/V = 2$:

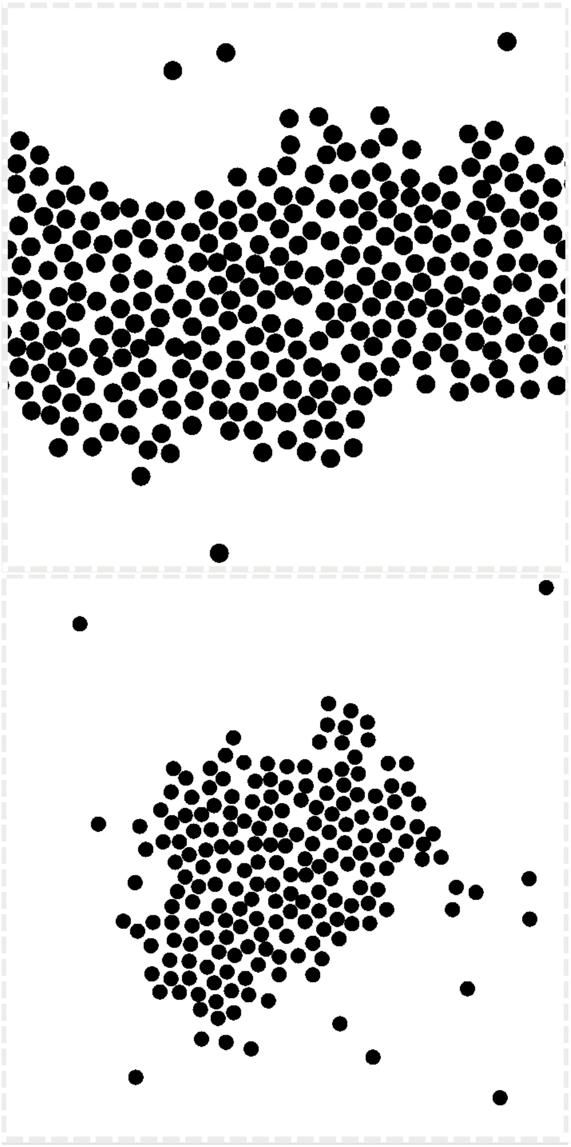
$$u_{\mathrm{wall}}(d) = \rho\pi\left(\frac{5}{24d^6} - \frac{1}{d^2}\right)$$

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 $_{\mathrm{at}}$)

Tasks

- In the slab geometry, determine the line tension of a 2D fluid (analogy of the surface tension in 2D), the density of liquid at slab center, and optionally (if you use $N > 400$ particles and density $\rho \le 0.25$) also the equilibrium vapor pressure.
- Unless you use a large system, determine the equilibrium vapor pressure using a slab geometry with two walls, cf. method described here.
- Determine the vapor pressure above a droplet and the droplet radius r.
- Verify whether the predicted vapor pressure matches the 2D Kelvin equation prediction.
- Optionally, repeat with vapor densities instead of pressure and with droplet density $N/\pi r^2$.
- Optionally, simulate a cavity and determine the vapor density in it. (Why it is not possible to calculate the pressure of vapor in a cavity from the total system pressure?)



Simulation methods

- The simulation starts from a random configuration using MC (to remove overlaps), then it automatically switches to MD. The leap-frog integrator is used.
- Recommended method for the equilibrium: Bussi thermostat; other methods incl. MC are possible, too.
- Diagonal pressure tensor components are calculated from the virial of force:

$$p_{xx} = \rho k_{\mathrm{B}} T + \frac{1}{DV}\left\langle \sum r_x f_x \right\rangle, \quad p_{yy} = \rho k_{\mathrm{B}} T + \frac{1}{DV}\left\langle \sum r_y f_y \right\rangle$$

$\rho = N/V$ = number density*,

$V = L^D$, L = edge length, D = dimension ($D = 2$),

the sum is over all pair forces (particle–particle, wall-particle).

- In the simulation between walls, pressure is determined from the averaged force on the top wall.
- For the slab geometry, the vapor pressure = p_{xx}, otherwise $p = (p_{yy} + p_{xx})/2$.
- The line (“surface”) tension in the slab geometry is $\gamma = L_y(p_{yy} - p_{xx})$
- The density profiles are automatically centered.

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

Kelvin equation in *n*D

$$\ln\left(\frac{p_r^{\mathrm{s}}}{p_\infty^{\mathrm{s}}}\right) = \pm\frac{(D-1)\gamma}{k_{\mathrm{B}}T\rho r}$$

p_r^{s} = vapor pressure above an r-droplet (+) or in an r-cavity (−)

p_∞^{s} = vapor pressure above a flat interface

γ = linear tension (2D), surface tension (3D)

r = radius (always positive)

D = dimension

Simplifications:

- Vapor is ideal gas.
- $r \gg$ molecule size.
- Droplet is homogeneous liquid.
- Linear tension does not depend on temperature.

SIMOLANT – installation (Windows)

- `http://old.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`

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”.
- 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..

Slab simulation – setup

- Menu: Prepare system → Horizontal Slab
- The default temperature T=0.6, default recommended thermostat Bussi CSVR[†].
  Optionaly, T in range from 0.5 (long runs needed) to 0.65 (less accurate)
- Default number of atoms = 300 should be OK, although it is better to use more (400–500).
  On a slow computer, decrease the number of atoms (slider “N”), but not below 250.
- The default overall density, $\rho = 0.3$, is acceptable.
  For higher N, a bit lower $\rho = 0.25$ or so is better to avoid mutual interaction of both surfaces in the y-periodic boundary conditions, but there is a danger of breaking the slab.
- 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)
- In the Expert panel, select include: Dens.prof.

Hint: Some speed can be gained by turning off drawing using selector draw mode: Nothing
Do not forget to return back to know what’s going on!

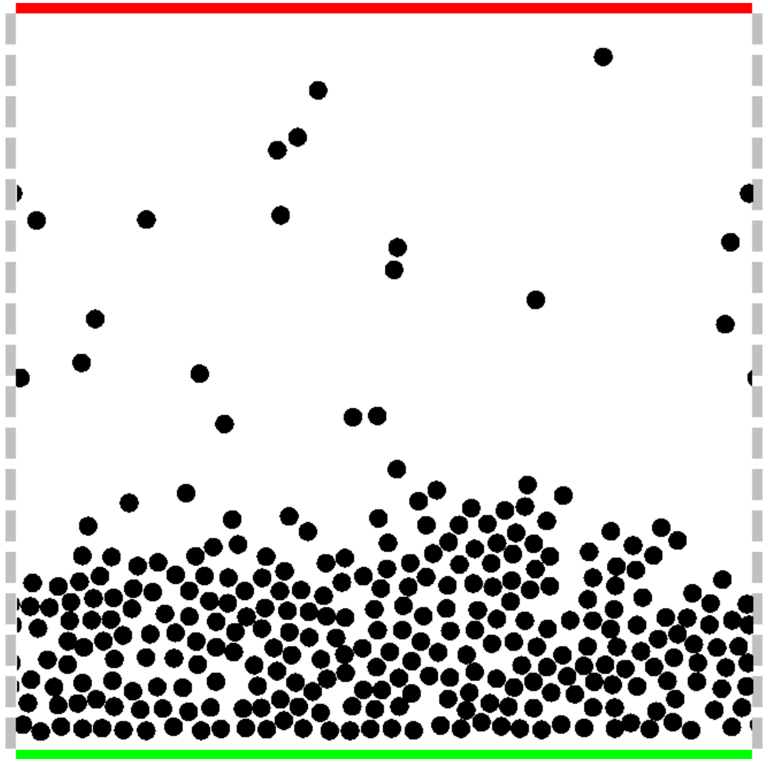
[†] Canonical Sampling through Velocity Rescaling

Simulation in the slab geometry

- Check optically whether the slab is stable and the density profile looks well.
- If you wish decimal commas in the recorded files (export to Czech excel), click ☐,.
- Click ☐record. Do not change simulation parameters during recording!
- If you will use the method with walls, accumulate at least 100 blocks (watch n=) – the more the better!
  If you use $N > 400$ and $\rho \leq 0.25$, use will need blocks, but may avoid the next step.
  Then click ☑record again and select “save”.

Simulation with walls

If the slab system is not large enough, both surfaces atract each other and decrease the measured pressure (systematic method error). Hence it is recommended to use a method with two walls, one attractive and one repulsive.



- Menu: Prepare system → Vapor-liquid equilibrium
- Set temperature to the same value as in the previous step
- Click ▮record
  accumulate enough blocks (100 or more)
  click ▮record again
  select append to “simolant.txt” and clear.
- In the second measurement block of `simolant.txt`, find value of `P(top wall)` – this is the measured vapor pressure.

Simulation of a droplet

- Decrease the number of atoms to about $N = 150$.
- Menu: Prepare system → Liquid droplet
- Check optically the droplet and set/verify the temperature (should be the same as before).
- Record the results by ▮record. When at least 50 blocks are finished, push ▮record again. Since file `simolant.txt` is present, you will be prompted by append to “simolant.txt” and clear.

Data analysis

The results are in file `simolant.txt`. You should find 2 or 3 data blocks headed with lines as:

```
=========== MEASUREMENT =========== # 1 ===========
```

- In block #1, find the following quantities (w. errors):
  Pyy = saturated pressure
  γ = line tension
- If you have run the system with two walls, use quantity P(top wall) in block #2 instead of Pyy from block #1.
- Draw the vertical density profile (= columns 1 and 2 marked as VDP1 in column 4) and determine (graphically) the averaged densities in liquid and gas, ρ^{l} and ρ^{g}. If you have run the system with two walls, try the table marked VDP2 from block #2.
- In the last block (#2 or #3), find Pvir = pressure (= average of Pxx and Pyy).
- Draw the radial density profile (columns 1 and 2 marked as DRDP(number) in column 4) and determine:
  ρ^{l}_r and ρ^{g}_r = averaged densities in liquid and gas,
  r = determine the droplet radius (r for which $\rho = (\rho^{\mathrm{l}}_r + \rho^{\mathrm{g}}_r)/2$).
- Using the cumulative density profile (columns 1 and 3 marked as DRDP(number) in column 4), determine the number of particles N_r in the r-disk.

Calculations

Pseudoexperiment

- Calculate with error estimate (p^{s}_{r} = Pvir, p^{s}_{∞} = Pyy or P(top wall))

$$\ln\left(\frac{p^{\mathrm{s}}_{r}}{p^{\mathrm{s}}_{\infty}}\right) \pm \sqrt{(\text{rel. error of } p^{\mathrm{s}}_{r})^2 + (\text{rel. error of } p^{\mathrm{s}}_{\infty})^2}$$

- Calculate the similar result based on vapor densities and compare with the above result.

$$\ln\left(\frac{\rho^{\mathrm{s}}_{r}}{\rho^{\mathrm{s}}_{\infty}}\right) \pm \sqrt{(\text{rel. error of } p^{\mathrm{s}}_{r})^2 + (\text{rel. error of } p^{\mathrm{s}}_{\infty})^2}$$

Kelvin prediction

- Calculate with the liquid density ρ^{l} from the slab:

$$\frac{\gamma}{k_{\mathrm{B}} T \rho^{\mathrm{l}} r}$$

- Recalculate with $\rho^{\mathrm{l}} = N_r/\pi r^2$, where N_r is the number of atoms in the r-disk.

If you have time – cavity

- Repeat with about $N = 300$ molecules and a cavity. Use:
  Menu: File → Bubble (cavity)
- Set the periodic boundary conditions:
  Menu: Boundary Conditions → Periodic
  (for smaller N, the default box with attractive walls may work, too)
- You may need to change the density to fine-adjust the cavity radius.