

Simulation study of the Kelvin equation in 2D

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

Software: SIMOLANT

Model: 8-4 type potential (\approx Lennard-Jones in 2D)

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

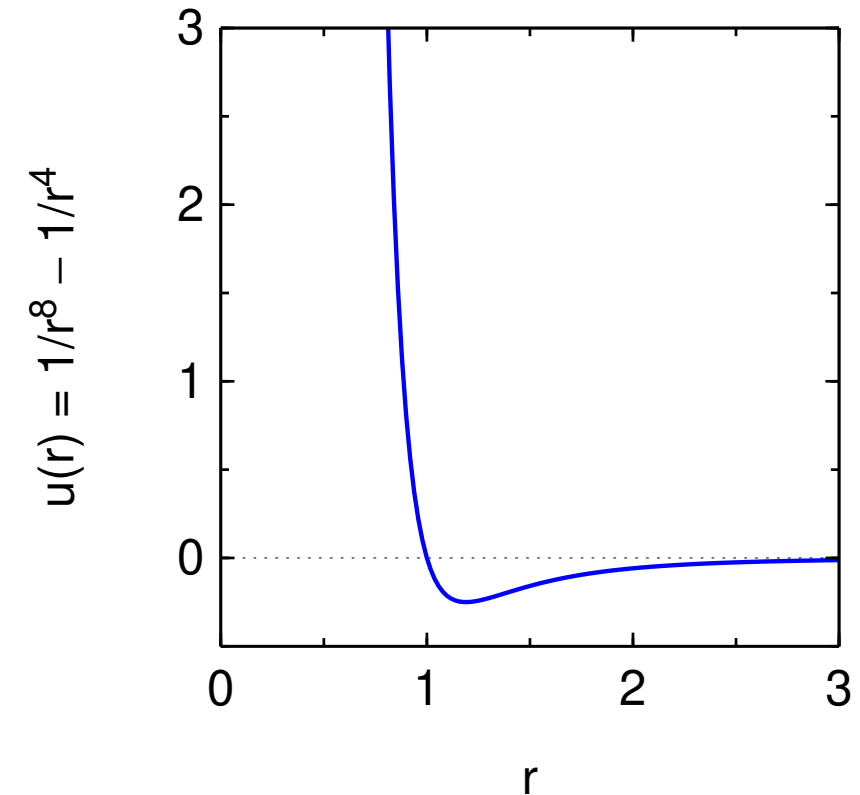
truncated at $r_c = 4$ and smoothly sewed in.

Attractive walls = potential u integrated over a continuous distribution of particles with number density $\rho = N/V = 2$:

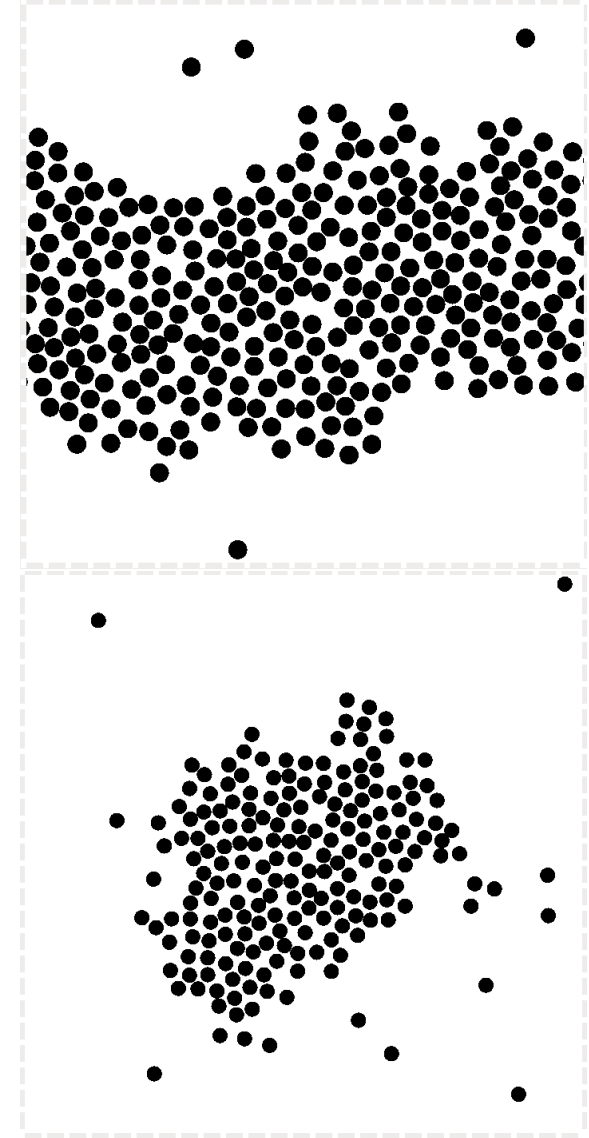
$$u_{\text{wall}}(d) = \rho\pi \left(\frac{5}{24d^6} - \frac{1}{d^2} \right)$$

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)



- 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 the equilibrium vapor pressure.
- Only in case you have a slow computer and therefore use less than 400–500 particles, one more step will be needed to determine the vapor pressure.
- Determine the vapor pressure above an r -droplet.
- Verify whether the predicted vapor pressure matches the 2D Kelvin equation prediction.
- Optionally, repeat with vapor densities instead of vapor pressures 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?)



- 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:

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

$\rho = N/V$ = 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.
- In the slab geometry, the vapor pressure = p_{yy} , 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

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

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 curvature.

- <https://github.com/kolafaj/SIMOLANT>
- Download `executables/simolant-win.zip`
- Create a folder and unpack SIMOLANT there.
Do not run directly from `simolant-win.zip` which in Windows is treated as a “folder”
- Run `simolant.exe`

Hints:


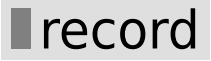
- The calculated data are exported to file `simolant.txt` with a decimal point. If you like decimal comma (useful with Czech localization), click , in panel “Measure”.
- If you restart SIMOLANT, the old `simolant.txt` would be overwritten. Either rename `simolant.txt` in advance, or change the export name by:
Menu: **File** → **Protocol name..**

Slab simulation – setup

- Menu: Prepare system → Horizontal Slab
- The default temperature $T=0.6$, default recommended thermostat Bussi CSV[†].
Optionally, T in range from 0.5 (long runs needed) to 0.65 (less accurate)
- Set the number of atoms (slider “N”) to at least 500.
On a slow computer, decrease the number of atoms, but not below 250.
- The overall density should be $\rho = 0.25$ (or a bit less for large N) to avoid mutual interaction of both surfaces in the y-periodic boundary conditions, but there is a danger of breaking the slab.
- For lower N , set $\rho = 0.3$. Another step to determine the vapor pressure will be needed.
- 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

- 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!**
- Accumulate at least 100 blocks (watch $n=$) – the more the better!
- for smaller number of particles, less blocks is needed, but you will have to run another simulation (see next slide).

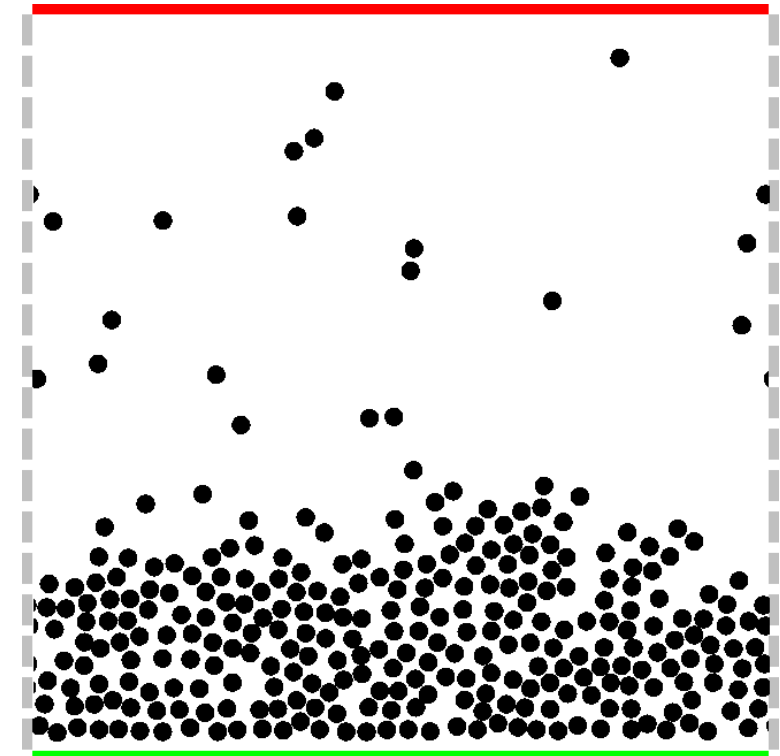
Then click  record again and select “save”.

Simulation with walls (needed for small N)

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If the slab system is not large enough (at least about $N = 500$), both surfaces attract 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 $P(\text{top wall})$ – this is the measured vapor pressure.



Simulation of a droplet

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- 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`.

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_r^l and ρ_r^g = averaged densities in liquid and gas,
 r = determine the droplet radius (r for which $\rho = (\rho_r^l + \rho_r^g)/2$).
- 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.

Pseudoexperiment

- Calculate with error estimate ($p_r^s = P_{\text{vir}}$, $p_\infty^s = P_{\text{yy}}$ or $P(\text{top wall})$)

$$\ln\left(\frac{p_r^s}{p_\infty^s}\right) \pm \sqrt{(\text{rel. error of } p_r^s)^2 + (\text{rel. error of } p_\infty^s)^2}$$

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

$$\ln\left(\frac{\rho_r^s}{\rho_\infty^s}\right) \pm \sqrt{(\text{rel. error of } p_r^s)^2 + (\text{rel. error of } p_\infty^s)^2}$$

Kelvin prediction

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

$$\frac{\gamma}{k_B T \rho^l r}$$

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

- 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.