

Verification of the Clausius–Clapeyron equation

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Aim: Verify the Clausius–Clapeyron equation by simulations 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.

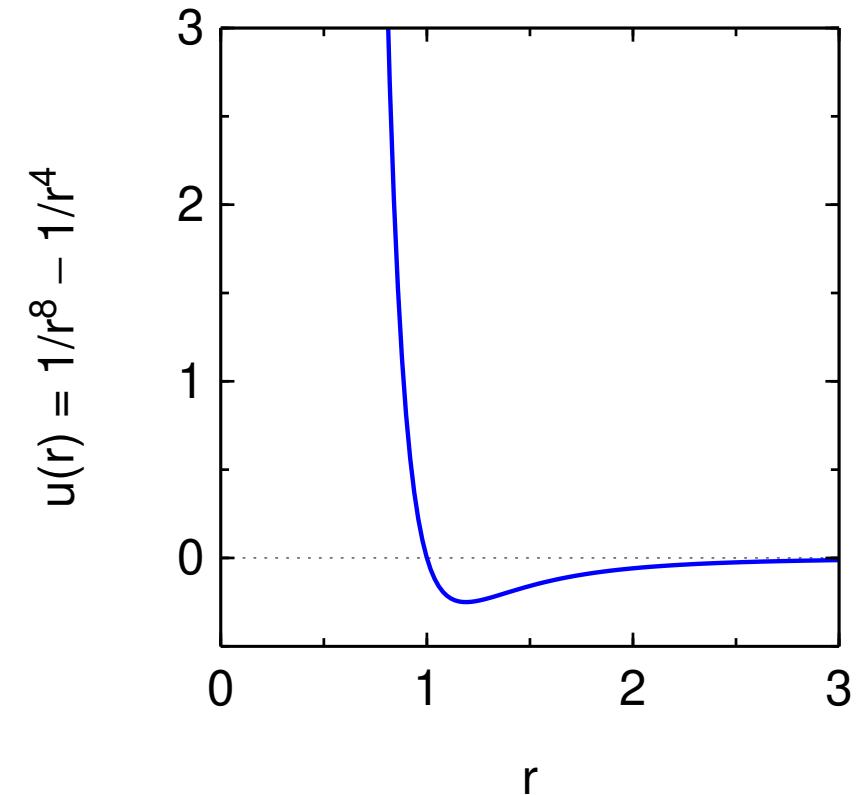
Attractive walls = potential u integrated over a continuous distribution of particles with number density $\rho = N/V = 0.75$:

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

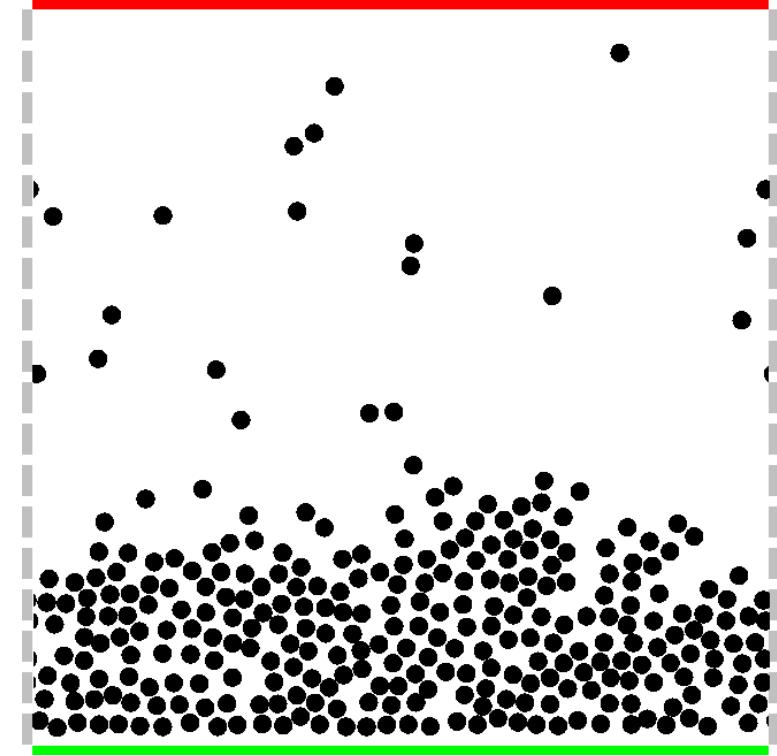
Repulsive walls do not contain $-\frac{1}{d^2}$

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)



- 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 conditions.
- Compare both values.



- 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):

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

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

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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 \ll vapor volume
- The ideal gas equation of state holds for the vapor phase.

In the simulation, the first two simplifications are valid ($\pm 2\%$), however, nonideality is sizeable ($\approx 30\%$ 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: ($k_B \equiv 1$)

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

Compressibility factor:

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

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

Vaporization enthalpy from NPT simulations of liquid and gas

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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:

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

Also, Z of vapor for the last step is determined

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

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

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

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

i.e., one simple NVT simulation suffices.

- <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!

^aBut not Minimum – nothing would be calculated!

The screenshot shows the MD/Bussi CSV software interface. On the left, a 3D visualization of a molecular system is shown with black spheres representing atoms. The main window displays simulation parameters and a plot of energy convergence. The parameters section includes:

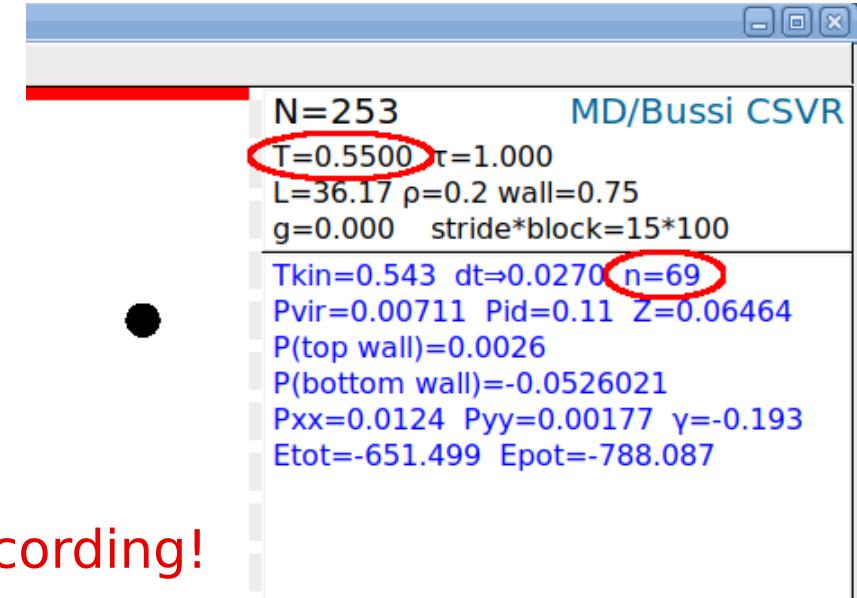
- N=253** (circled in red)
- T=0.500 τ =1.000
- L=36.17 ρ =0.2 wall=0.75
- g=0.00 stride*block=15*100 (circled in red)
- Tkin=0.659 τ =0.0248
- Pvir=0.01656 Pid=0.13 Z=0.1274
- Etot=-517.575 Epot=-683.74

The plot shows the convergence of energy (Epot+Ekin) over time, with a maximum-minimum range of 60.19. The plot area is highlighted with a red oval. Below the plot, the 'Parameters' section has sliders for T, τ , g, ρ , and N, with the N slider also circled in red. The 'Walls' section has checkboxes for 'top' and 'bottom', with 'bottom' checked. The 'Expert' section has a 'record' checkbox and a dropdown menu for 'include' set to 'Nothing'. The 'molecule size' is set to 'Real', 'draw mode' to 'Movie', and 'color mode' to 'Black'. The 'run' button is highlighted with a red oval. At the bottom, the 'simulation speed' and 'measurement block' sliders are circled in red.

Vapor pressure – simulation #1 at T_1

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- 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: +



```
N=253 MD/Bussi CSVR
T=0.5500  $\tau$ =1.000
L=36.17  $\rho$ =0.2 wall=0.75
g=0.000 stride*block=15*100
Tkin=0.543 dt=0.0270 n=69
Pvir=0.00711 Pid=0.11 Z=0.06464
P(top wall)=0.0026
P(bottom wall)=-0.0526021
Pxx=0.0124 Pyy=0.00177  $\gamma$ =-0.193
Etot=-651.499 Epot=-788.087
```

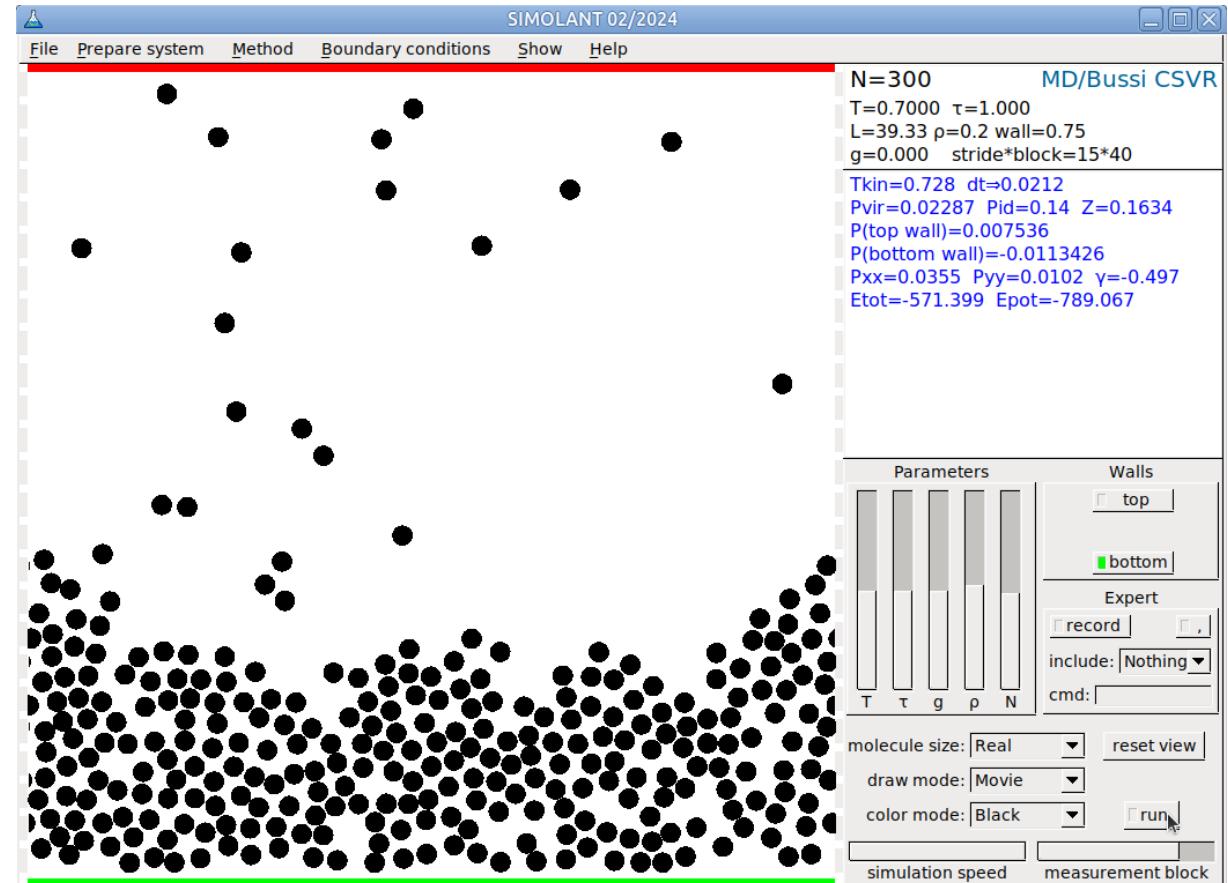
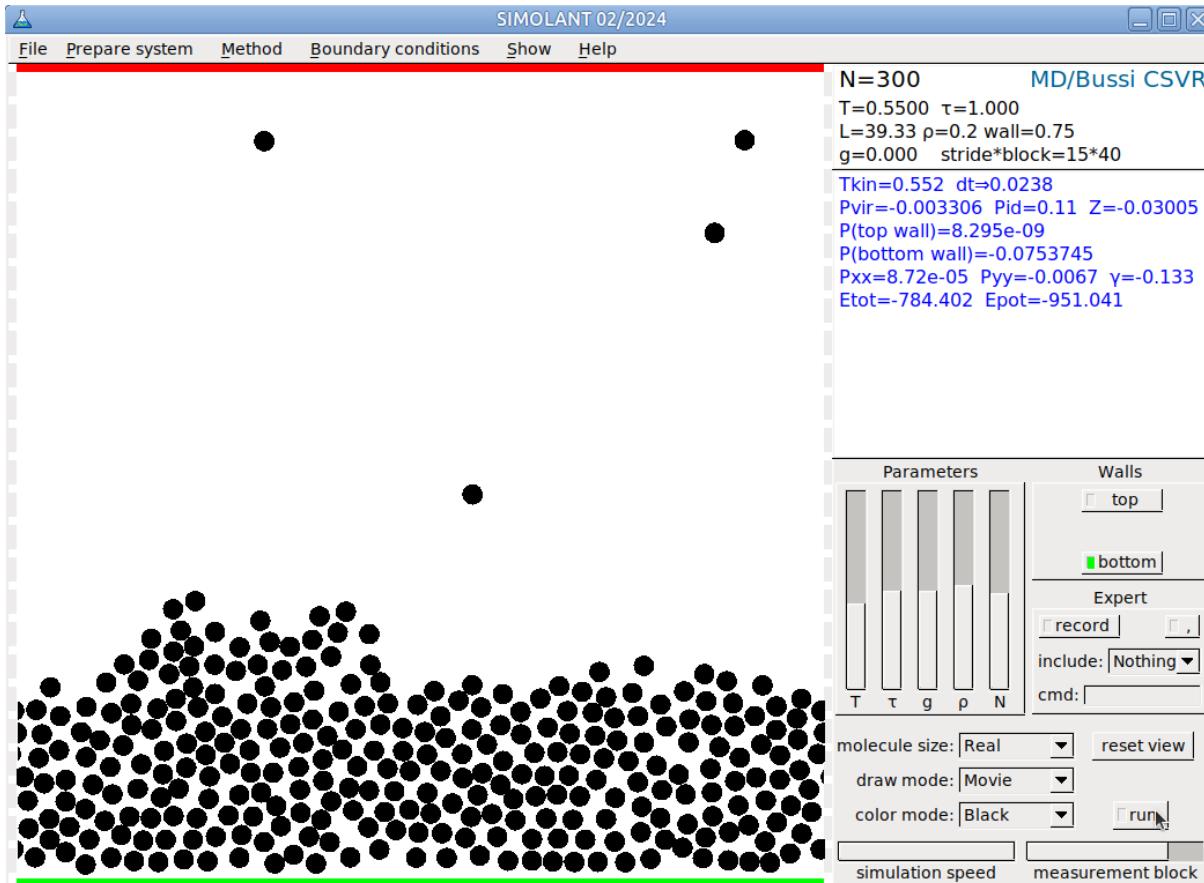
- Simulate until the system is equilibrated
- Click . **Do not change simulation parameters during recording!**
- After a while, click again. The results will be shown. The recommended number of blocks (n = right top) is at least 50, better over 100. The relative standard error of quantity $P(\text{top wall})^\dagger$, as given in (), should be less than 10%.
 - If not accurate enough, select .
 - If OK, select .

[†]optionally Pyy

Vapor pressure – simulation #2 at T_2

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- 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 to append to “simolant.txt” and clear



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:

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

Note the geometric mean for pressure – the pressure–temperature dependence is exponential.

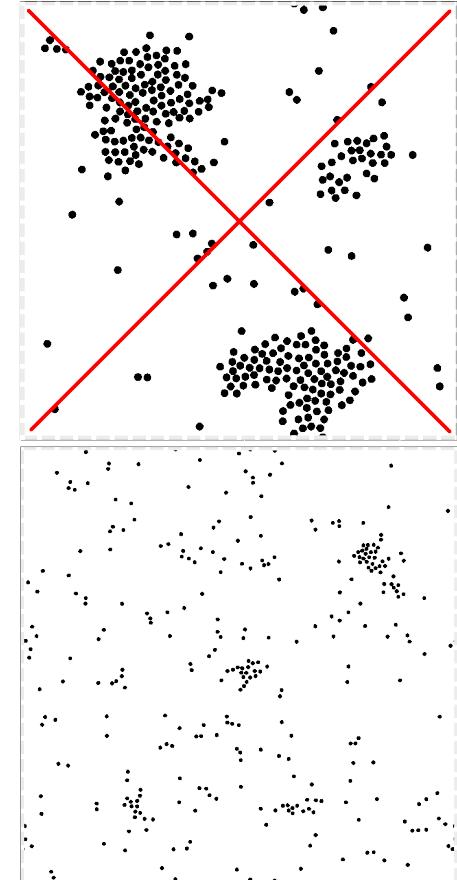
Be careful, in case of a wrong value, the subsequent simulations would be wrong!

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

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

- Menu: Boundary conditions → Periodic
- Set temperature to $\bar{T} = (T_1 + T_2)/2$ using cmd: `T=number` + `Enter`
- Set pressure to $\bar{p} = \sqrt{p_1 p_2}$: `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!

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

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

- 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.

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

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

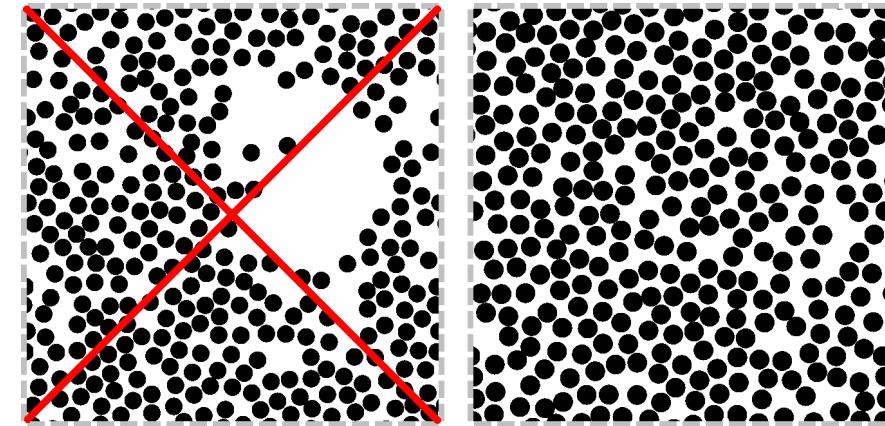
[‡]Standard error = estimated standard deviation of the average caused by stochastic noise. *Uncertainty* includes both the stochastic and systematic errors.

Vaporization enthalpy from *NPT* simulations #3 and #4

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Repeat the calculation of page 11 for liquid (simulation #4). You have already set the periodic boundary conditions, 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 \bar{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



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

- Calculate the vaporization enthalpy $\Delta_{\text{vap}}H_{\text{at}} = \frac{H(\text{g}) - H(\text{l})}{N}$ and its standard error

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

- 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?