Metropolis Monte- Carlo simulation of a Lenard-Jones fluid

The potential

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

① Reduced units

Multiply by
- mass m (kg)
- particle radius σ (m)
- potential depts ε (J)

to make dimensionless.

$$[J] = N \cdot m = \frac{m^2 \cdot kg}{s^2}$$

$$\rightarrow E^* = \frac{E}{\varepsilon}$$

$$\rightarrow [p] = \frac{N}{m^2} = \frac{\frac{m}{s^2} \cdot kg}{m^2} \Rightarrow \frac{m s^2}{kg} = \frac{s^2}{m^2 \cdot kg} \cdot m^3$$

$$p^* = \frac{p \cdot \sigma^3}{\varepsilon}$$

$$\rightarrow [t] = s \Rightarrow \ldots \quad \frac{1}{s} = \sqrt{\frac{m^2 \cdot kg}{s^2}} \cdot \sqrt{\frac{1}{kg}} \cdot \frac{1}{m}$$

$$t^* = t\,\sqrt{\varepsilon \cdot m} \cdot \frac{1}{\sigma}$$

$$\rightarrow [\eta] = \frac{kg}{m \cdot s} \Rightarrow \frac{m \cdot s}{kg} = \sqrt{\frac{s^2}{m^2\,kg} \cdot \frac{1}{kg}} \cdot m^2$$

$$\eta^* = \eta\,\frac{\sigma^2}{\sqrt{\varepsilon \cdot m}}$$

$$\rightarrow [S] = \frac{kg\ m^2}{s} \Rightarrow \frac{s}{kg \cdot m^2} = \sqrt{\frac{s^2}{m^2\,kg}} \cdot \sqrt{\frac{1}{kg}} \cdot \sqrt{\frac{1}{m}}$$

$$s^* = S \cdot \sqrt{\frac{\varepsilon}{m \cdot \sigma}}$$

how

$$\rightarrow [q] = A \cdot s \Rightarrow \frac{1}{s} =$$

$$q^* = q/e \qquad e = 1{,}6 \cdot 10^{-19}$$

Using the optimal parameters:

$$p^* = 1 \ \ldots \ p^* = \frac{p \cdot \sigma^3}{\varepsilon} \Rightarrow p = \frac{p^*\,\varepsilon}{\sigma^3} = \frac{1 \cdot 119{,}8 \cdot k_B}{3{,}405 \cdot 10^{-10}} = \underline{4{,}8576 \cdot 10^{-12}}$$

$$t^* = 0{,}005 \ \ldots \ t^* = t\,\frac{\sqrt{\varepsilon m}}{\sigma} \Rightarrow t = t^*\,\frac{\sigma}{\sqrt{\varepsilon m}} = \underline{\underline{1{,}197065 \cdot 10^{-35}}}$$

(c)

	expected	LAMMPS unit	conversion
length	A.	Angstroms	10^{-10}
time	ps	femtoseconds	10^{-15}
mass	g/mol	grams/mole	$10^{-3} N_A$
Force	$A \cdot \frac{g}{mol} \cdot \frac{1}{ps^2} = \frac{A \cdot g}{ps^2} \cdot \frac{1}{mol}$	kcal/mole · Angstrom	2.3809523809523812e+23

$$\underbrace{\frac{10^{-10} \cdot 10^{-3}}{(10^{-12})^2}}_{\text{To base SI}} \cdot \underbrace{\frac{1}{4200}}_{\text{Joule} \downarrow \text{kcal}} \cdot \underbrace{\frac{1}{10^{-10}}}_{\text{Angstr} \downarrow \text{meter}} = 2{,}3 \cdot 10^{23}$$

energy $\quad A^2 \frac{g}{mol} \frac{1}{ps^2} = \frac{A^2 \cdot g}{ps^2} \cdot \frac{1}{mol} \quad$ kcal/mole

$$\underbrace{\frac{10^{-10} \cdot 10^{-3}}{(10^{-12})^2}}_{\text{To base SI}} \cdot \underbrace{\frac{1}{4200}}_{\text{Joule} \downarrow \text{kcal}} = 2{,}3 \cdot 10^{23}$$

(d) Num val which corresponds to 1 atm.

1

(e) Value of $\hbar$

$1 \text{ J}\cdot\text{s} \; --- \; \frac{kcal}{mol \cdot A} \cdot ps \; .. \;$ conversion to real $\underline{\underline{2{,}38 \cdot 10^{11}}}$

$\hbar = 251.08852801098965 \frac{kcal}{mol \cdot A}$

(2) Basic LJ MC Simulation

Rho -?

$\rho = \frac{m}{L^3} =$

Simulation parameters

n=256
rho=0.03541076487252125
t=83.8
disp=0.3
dr=0.005
ntskip=1
ntprint/ntskip=1
ntjob/ntskip=100

After running the mclj:

```
Time    Accc rat. Pot eng/part     pressure
 100  3.12500e-01 -5.31262e+00  2.18082e+00
 200  3.59375e-01 -5.43905e+00  1.41181e+00
 300  3.78906e-01 -5.35583e+00  1.89036e+00
 400  3.12500e-01 -5.40607e+00  1.71707e+00
 500  3.51562e-01 -5.39238e+00  1.75051e+00
 600  4.21875e-01 -5.30287e+00  2.20873e+00
 700  3.24219e-01 -5.36869e+00  2.01023e+00
 800  3.51562e-01 -5.38203e+00  1.87002e+00
 900  3.47656e-01 -5.36842e+00  1.94168e+00
1000  3.63281e-01 -5.33981e+00  2.07724e+00
1100  4.06250e-01 -5.24661e+00  2.46898e+00
1200  3.71094e-01 -5.29613e+00  2.30097e+00
1300  3.24219e-01 -5.36709e+00  1.81460e+00
1400  3.55469e-01 -5.37075e+00  1.86762e+00
1500  3.55469e-01 -5.29154e+00  2.26118e+00
1600  3.59375e-01 -5.42252e+00  1.56773e+00
1700  3.00781e-01 -5.40009e+00  1.88108e+00
1800  3.47656e-01 -5.39119e+00  1.87119e+00
1900  3.12500e-01 -5.35310e+00  2.03715e+00
2000  3.78906e-01 -5.38604e+00  1.78849e+00
2100  4.06250e-01 -5.48131e+00  1.35122e+00
2200  3.98438e-01 -5.41961e+00  1.93039e+00
2300  3.67188e-01 -5.43137e+00  1.71133e+00
2400  3.12500e-01 -5.38463e+00  1.97377e+00
2500  3.12500e-01 -5.21260e+00  2.58764e+00
2600  3.47656e-01 -5.28610e+00  2.46794e+00
2700  3.94531e-01 -5.40122e+00  1.65772e+00
2800  4.17969e-01 -5.39906e+00  1.74854e+00
2900  3.35938e-01 -5.36630e+00  1.80730e+00
3000  3.47656e-01 -5.26940e+00  2.53787e+00
3100  3.20312e-01 -5.26893e+00  2.27362e+00
3200  3.63281e-01 -5.26699e+00  2.41298e+00
3300  4.06250e-01 -5.32244e+00  2.16367e+00
3400  3.47656e-01 -5.34304e+00  2.12308e+00
3500  3.04688e-01 -5.39852e+00  1.77237e+00
3600  3.63281e-01 -5.35918e+00  2.03257e+00
3700  3.55469e-01 -5.39559e+00  1.89124e+00
3800  3.59375e-01 -5.31962e+00  2.07099e+00
3900  3.94531e-01 -5.36480e+00  1.93615e+00
4000  3.16406e-01 -5.29166e+00  2.35667e+00
4100  3.51562e-01 -5.40263e+00  1.73566e+00
4200  3.63281e-01 -5.41082e+00  1.71198e+00
4300  3.59375e-01 -5.35377e+00  1.85392e+00
4400  3.67188e-01 -5.24837e+00  2.43367e+00
4500  3.55469e-01 -5.31111e+00  2.16672e+00
4600  3.63281e-01 -5.38682e+00  1.91247e+00
4700  3.47656e-01 -5.36792e+00  1.81291e+00
4800  4.14062e-01 -5.37861e+00  1.83789e+00
4900  3.43750e-01 -5.38933e+00  1.99398e+00
5000  3.59375e-01 -5.42006e+00  1.68267e+00
```

Output of the simulation

```
(base) jakub.dokulil@nbm-imp-134 lj-canonical % ./
amclj
 fname=[mclj_out.dat]

     n=       256
   rho=  0.80000
     t=  1.20000
  disp=  0.30000

    nt=         5000 (*    1)
  accr= 3.56287e-01.
 <U>/N=-5.36650e+00  ← potential energy
  Cv/N= 2.32938e+00
     p= 1.93203e+00
```

For comparison, the experimental values for pressure and potential energy of the liquid phase of argon at the triple point is p = 0.689 bar and U = −5.97kJ mol−1. The configurational part of the specific heat (i. e. excluding the contributions from kinetic energy) is CV′ = 6.9 J K−1 mol.