SHEET 9

(a) $[E] = kg \frac{m^2}{s^2}$ $\quad [v] = \sqrt{\frac{[E]}{[m]}} = \frac{m}{s}$

$$\Rightarrow [v'] = \sqrt{\frac{[E']}{[m']}} = \sqrt{\frac{[E]/\varepsilon}{[m]/\alpha}} = \sqrt{\frac{\alpha}{\varepsilon}}\,[v] = \frac{[v]}{\sqrt{\frac{\varepsilon}{\alpha}}} = \frac{[v]}{\sigma}$$

where α is the mass unit and ε the energy unit

(h) $\frac{1}{2} m v^2 = \frac{1}{2} k_B T \Rightarrow v = \sqrt{\frac{k_B T}{m}}$

$$\Rightarrow \frac{v'}{v} = \sqrt{\frac{T'}{T}}$$

(i) $\langle x_i \frac{\partial H}{\partial x_i} \rangle = k_B T$ $\quad x_i \begin{cases} q^i \\ p_i \end{cases}$

$H = E_K + V$ $\quad \frac{\partial H}{\partial q^i} = \frac{\partial V}{\partial q^i}$ $\quad \frac{\partial H}{\partial p_i} = \frac{\partial E_K}{\partial p_i}$

$$\langle p_i \frac{\partial H}{\partial p_i} \rangle = \langle p_i \frac{\partial E_K}{\partial p_i} \rangle = \langle \frac{p_i^2}{m} \rangle = k_B T$$

Summing over all particles and directions

$$\sum_{i=1}^{3N} k_B T = 3N k_B T = \sum_{i=1}^{3N} \langle \frac{p_i^2}{m} \rangle = \sum_{i=1}^{N} \langle \frac{p_{i,x}^2}{m} \rangle + \langle \frac{p_{i,y}^2}{m} \rangle + \langle \frac{p_{i,z}^2}{m} \rangle$$

Assuming $\langle p_x^2 \rangle = \langle p_y^2 \rangle = \langle p_z^2 \rangle$

$$\frac{3}{2} N k_B T = \frac{3}{2} \sum_{i=1}^{N} \frac{N}{N} \langle \frac{p_i^2}{m} \rangle = \langle E_K \rangle$$

Where I used that $N \left(\frac{1}{N} \sum_{i=1}^{N} 3 \langle \frac{p_i^2}{m} \rangle \right) = N \langle E_K^{Part} \rangle = \langle E_K \rangle$

Hence $C_v = \frac{1}{n} \frac{\partial U}{\partial T} = \frac{3}{2} R$ only when $U \approx E_K$

n = number of moles

Numerically, we can calculate C_v as follows:

$$C_v = \frac{\varepsilon}{n} \frac{U(T+\Delta T) - U(T)}{\Delta T} =$$

$$= \frac{120\,K \cdot k_B}{10\,K} \overset{n}{\left(\frac{N_A}{N}\right)} \Delta U =$$

$$= 12 \cdot \overset{k_B}{\left(\frac{R}{N_A}\right)} \frac{N_A}{N} \Delta U = \frac{12\,\Delta U\, R}{N}$$

We have $N = 8^3 = 512 \Rightarrow C_v / R = \frac{12\,\Delta U}{512} \simeq 0.0234\,\Delta U$

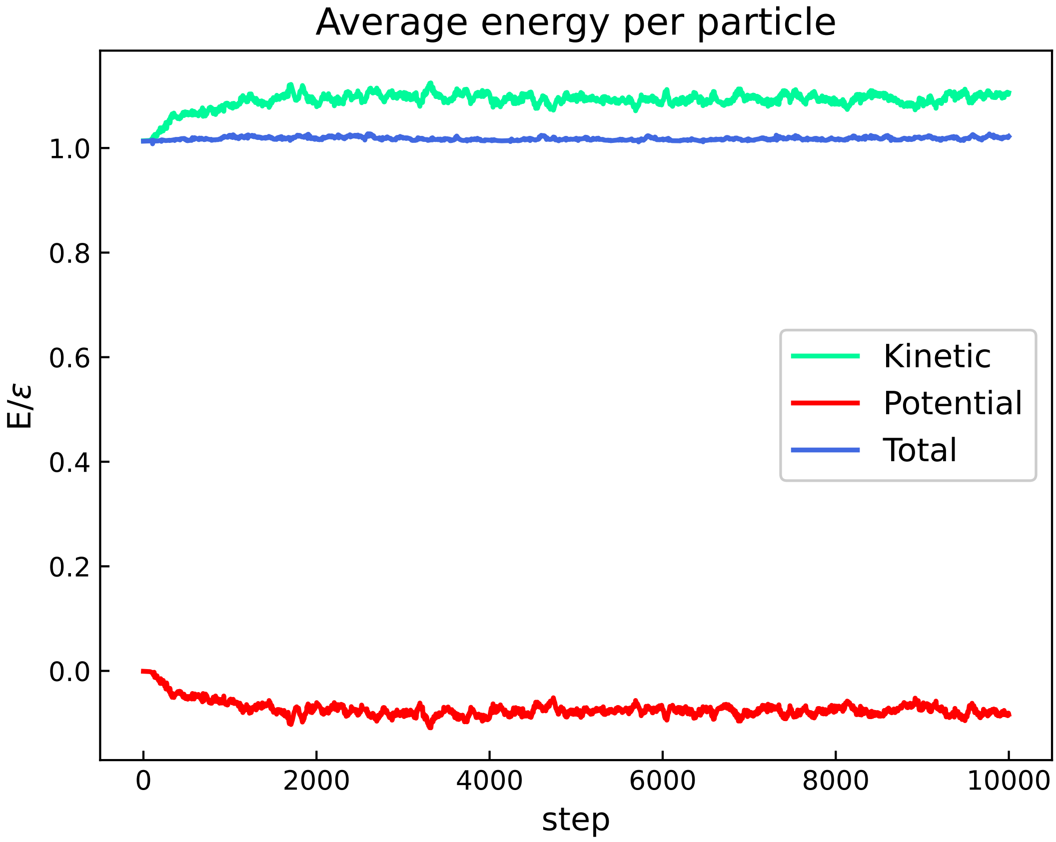
ΔU in natural units

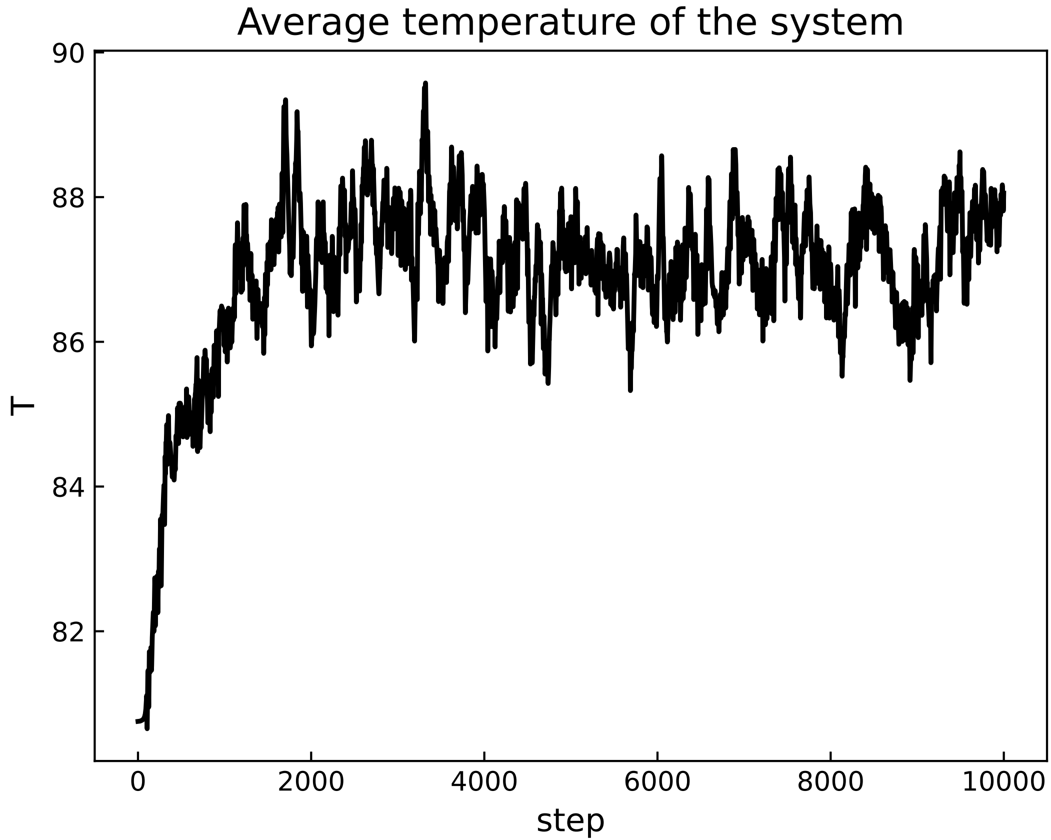
$$\frac{C_v}{R}(T = 75\,K) \simeq 1.55$$

$$\frac{C_v}{R}(T = 400\,k) \simeq 1.51$$

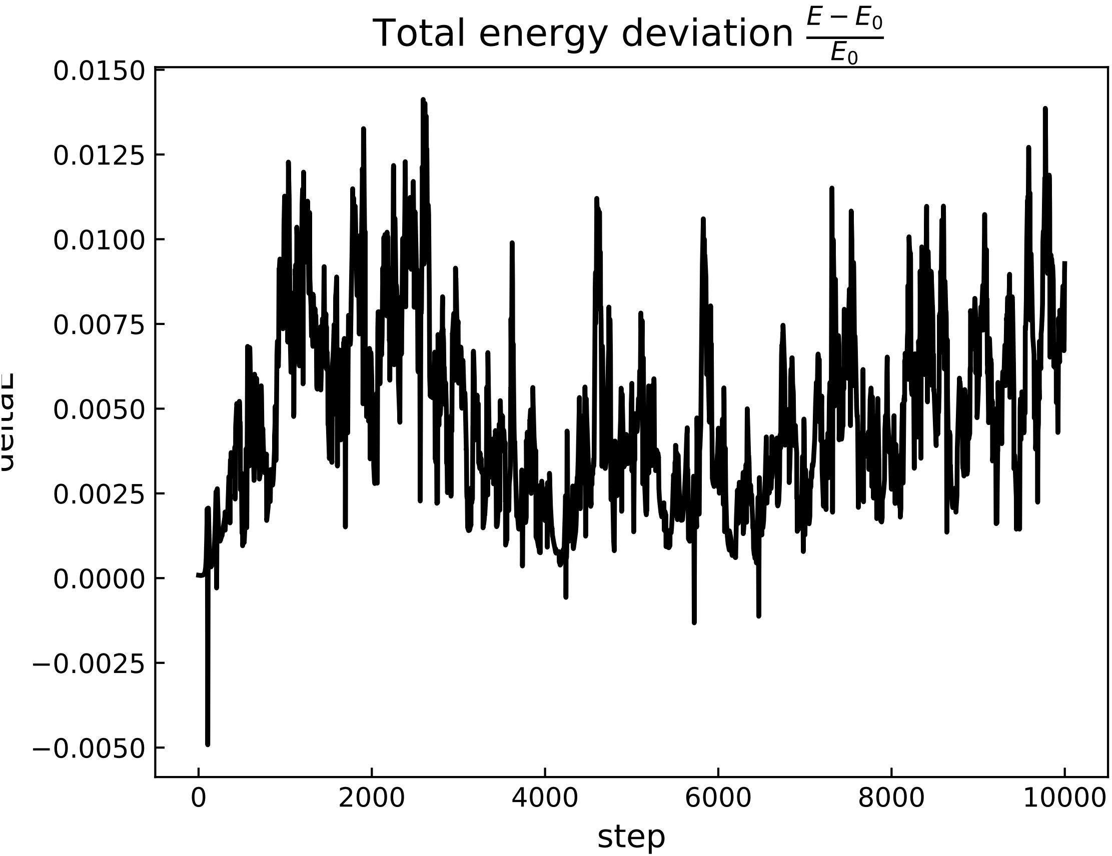
As the temperature grows so it does the kinetic energy.
Hence the approximation $U \simeq E_K$ becomes more accurate
(remember tha $C_v = \frac{3}{2}R$ only if $V=0$)

(j) The temperature is so low that the contribution to the total energy of the system comes almost only from the potential.
We expect the particles to lie at an average distance equal to the equilibrium ~~point~~ distance of the Lennard-Jones potential, since temperature does not provide enough excitation to jump away
we also expect C_v very different from $\frac{3}{2}R$

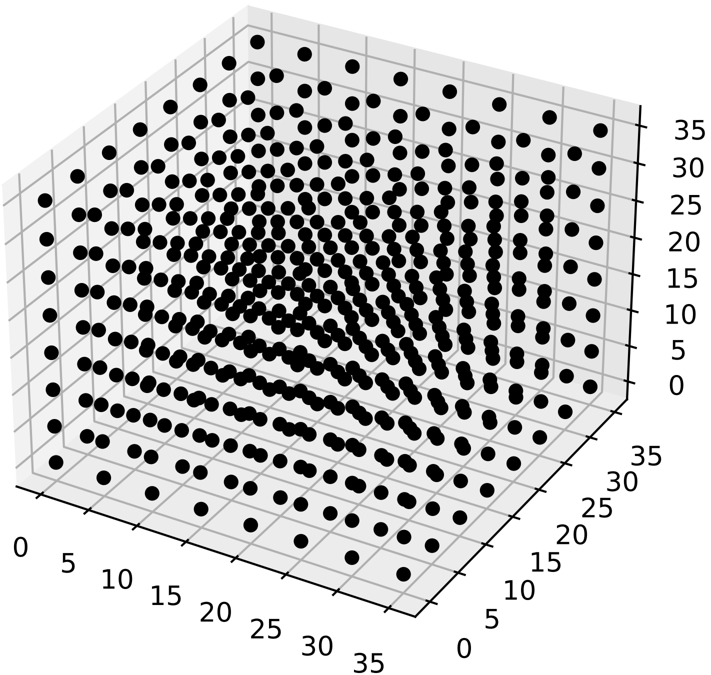

Average energy per particle
E/ε
step
Kinetic
Potential
Total
1.0
0.8
0.6
0.4
0.2
0.0
0
2000
4000
6000
8000
10000



Average temperature of the system
90
88
86
84
82
T
0
2000
4000
6000
8000
10000
step



Total energy deviation $\frac{E-E_0}{E_0}$
0.0150
0.0125
0.0100
0.0075
0.0050
0.0025
0.0000
−0.0025
−0.0050
0
2000
4000
6000
8000
10000
step



0
5
10
15
20
25
30
35
0
5
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15
20
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30
35
0
5
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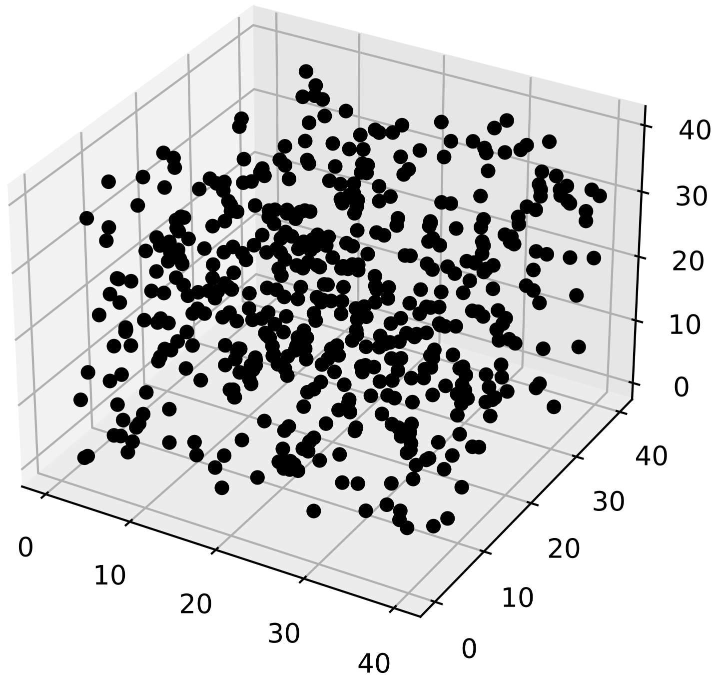
35



0
10
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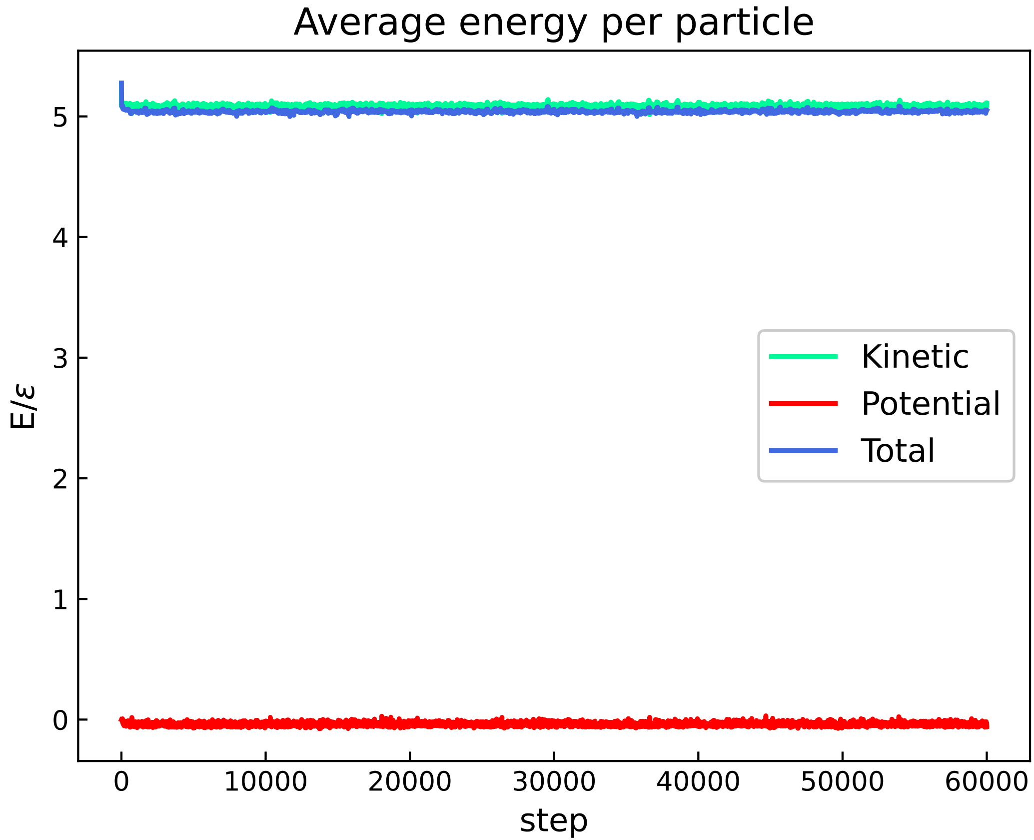
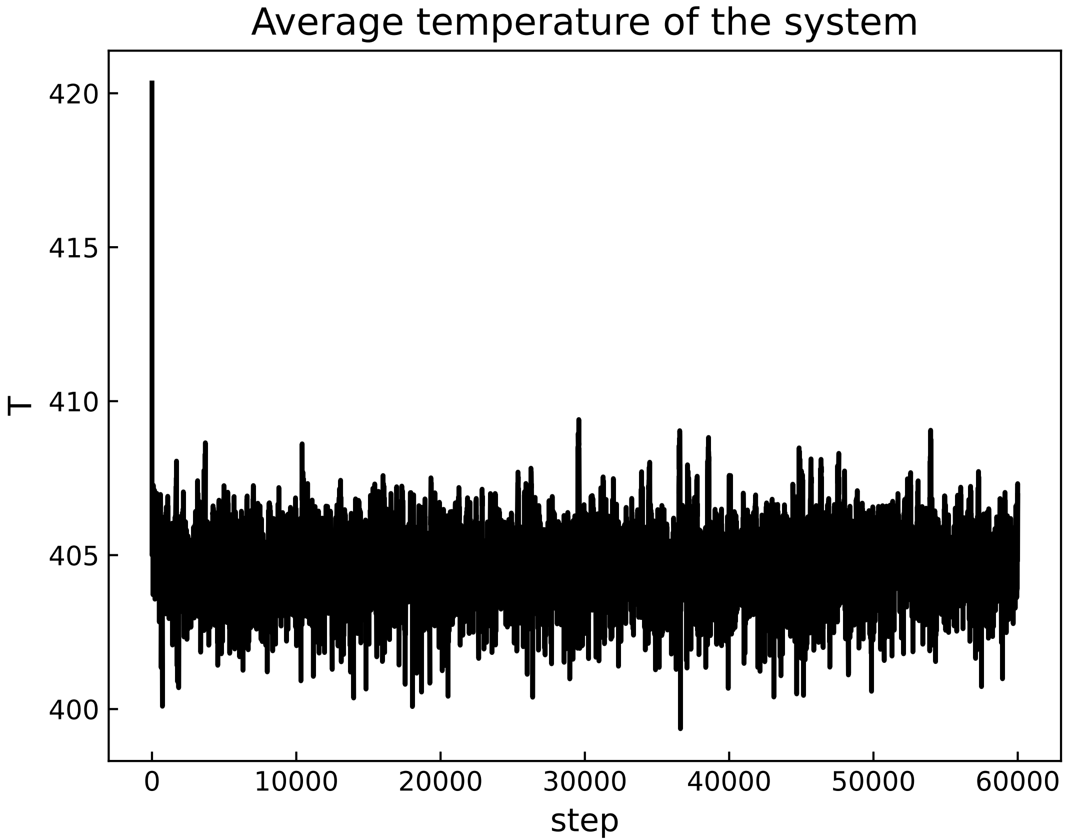
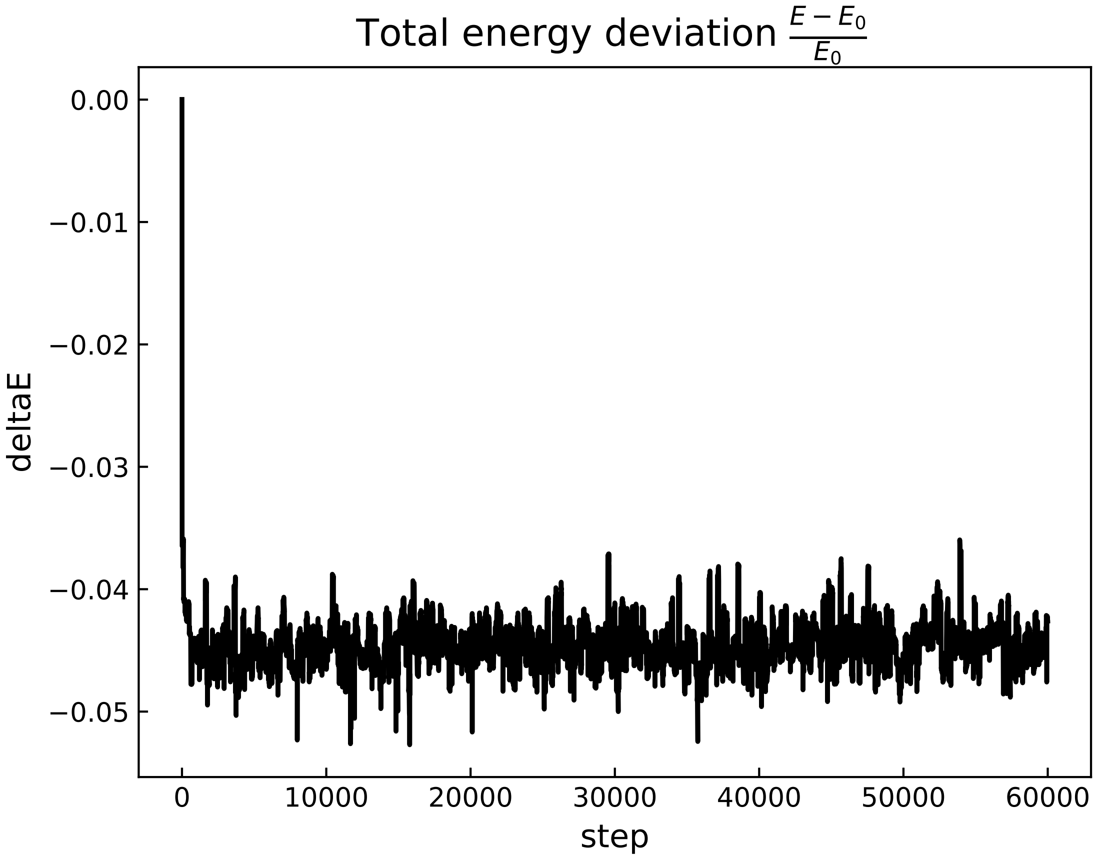
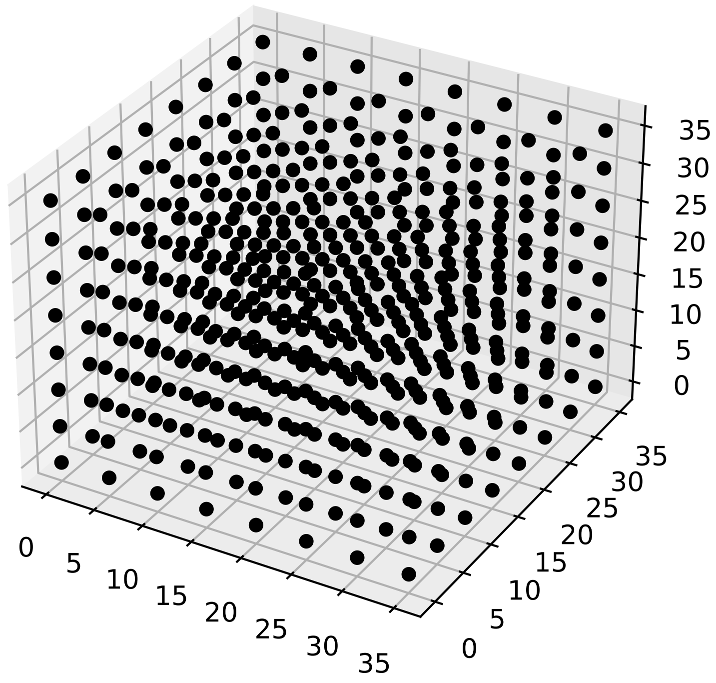

Average energy per particle
E/ε
step
Kinetic
Potential
Total
0
1
2
3
4
5
0
10000
20000
30000
40000
50000
60000


Average temperature of the system
T
420
415
410
405
400
0
10000
20000
30000
40000
50000
60000
step



Total energy deviation $\frac{E-E_0}{E_0}$
0.00
−0.01
−0.02
−0.03
−0.04
−0.05
deltaE
0
10000
20000
30000
40000
50000
60000
step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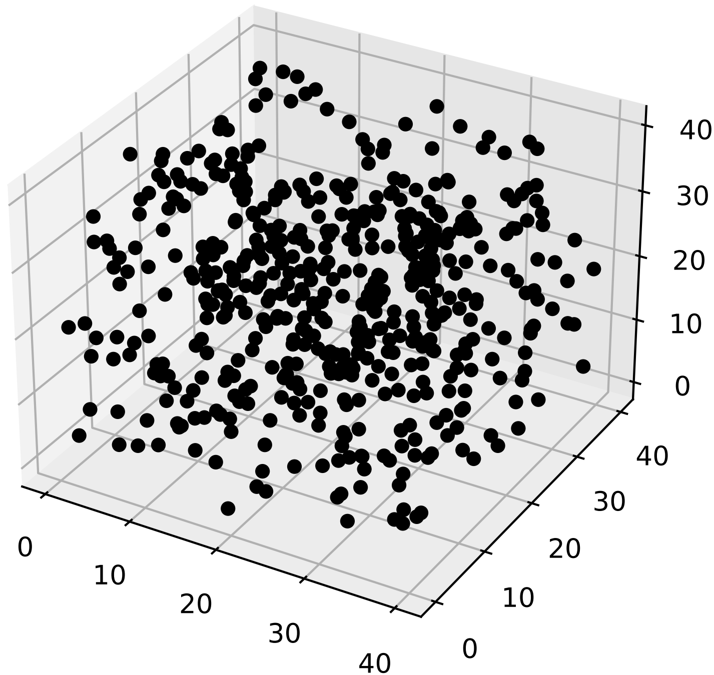

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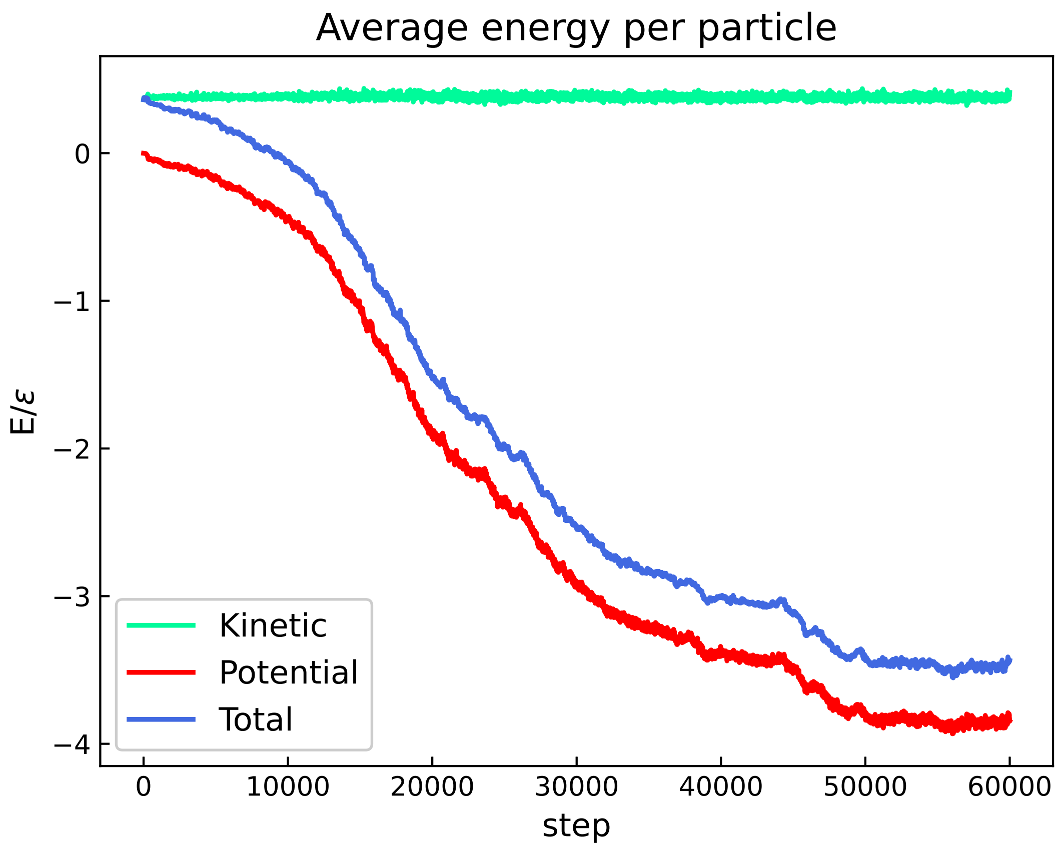
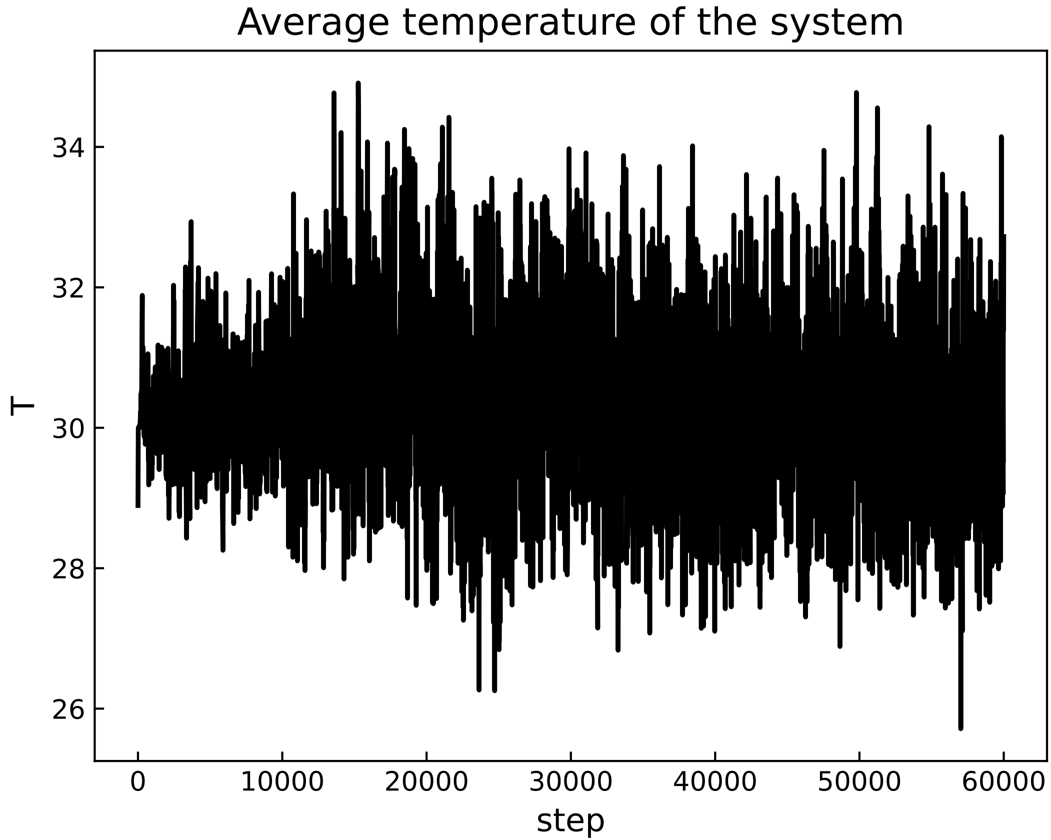
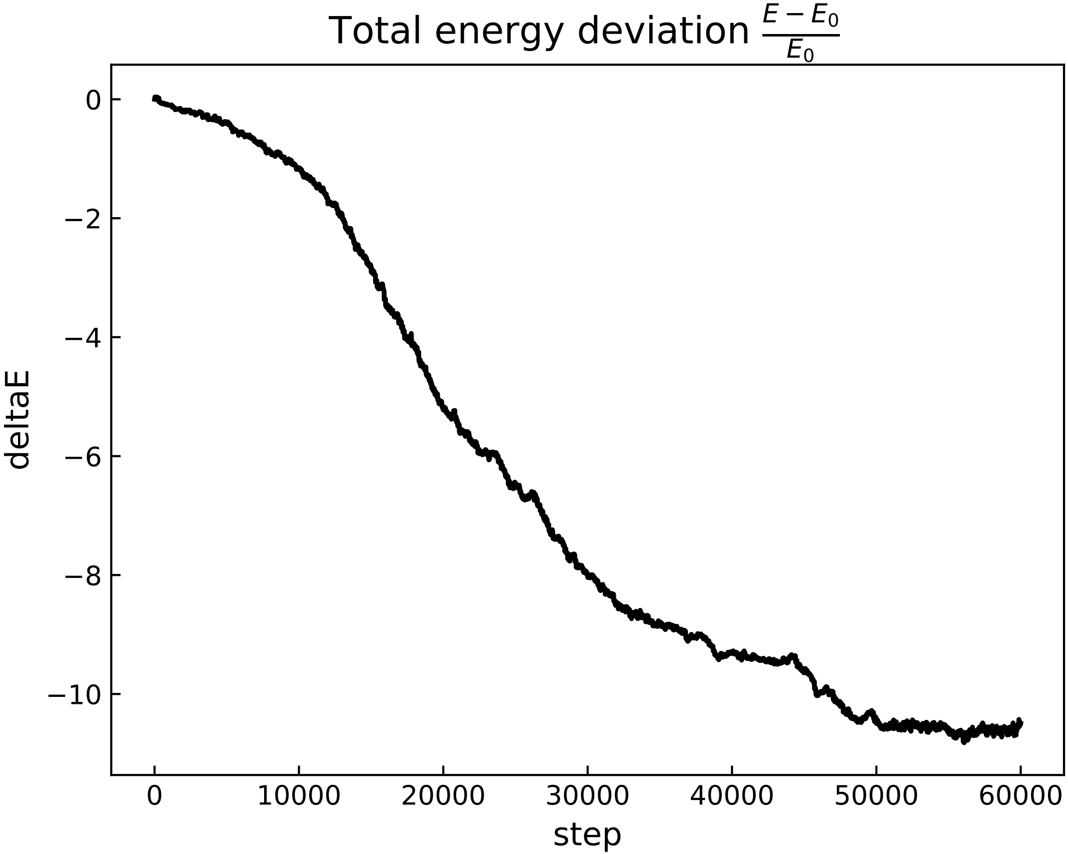
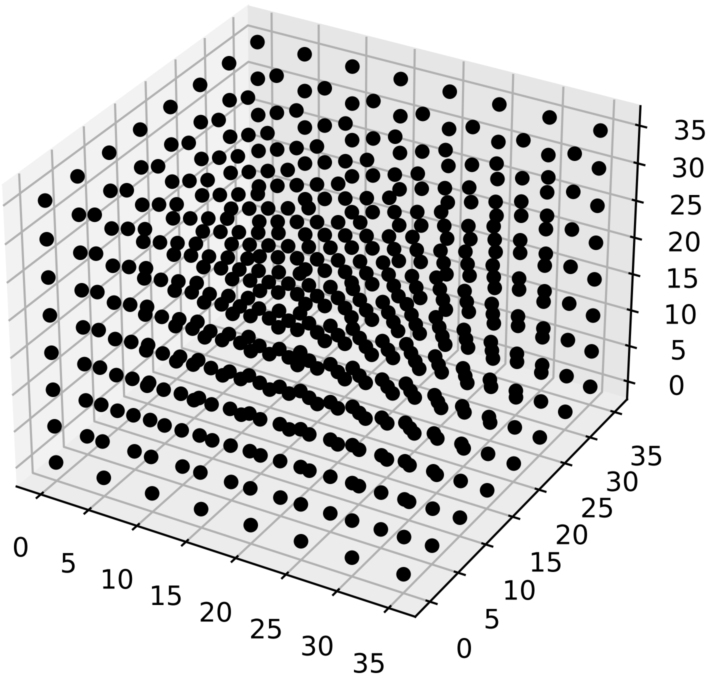

Average energy per particle
E/ε
step
0
−1
−2
−3
−4
0
10000
20000
30000
40000
50000
60000
Kinetic
Potential
Total



Average temperature of the system
T
step
34
32
30
28
26
0
10000
20000
30000
40000
50000
60000



Total energy deviation $\frac{E-E_0}{E_0}$
deltaE
step
0
−2
−4
−6
−8
−10
0
10000
20000
30000
40000
50000
60000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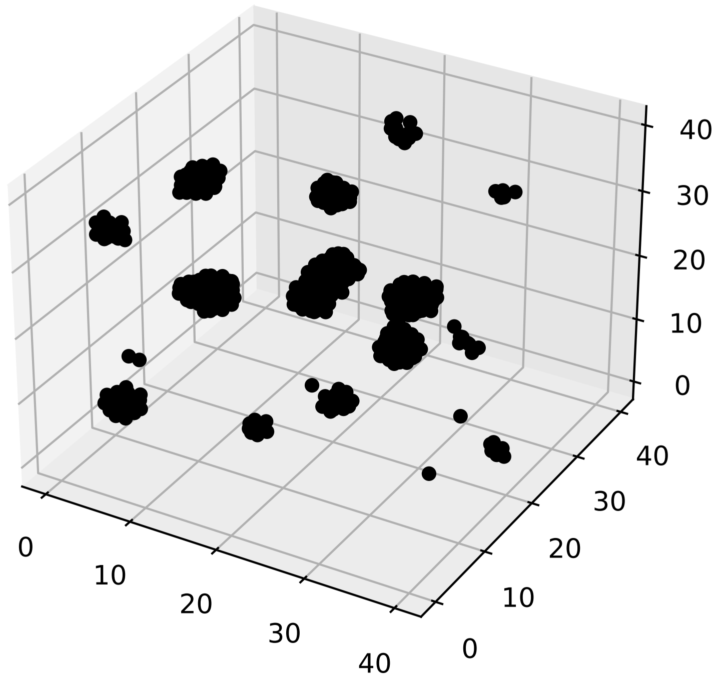

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