Molecular Dynamics

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The state qualification exam in Physics,
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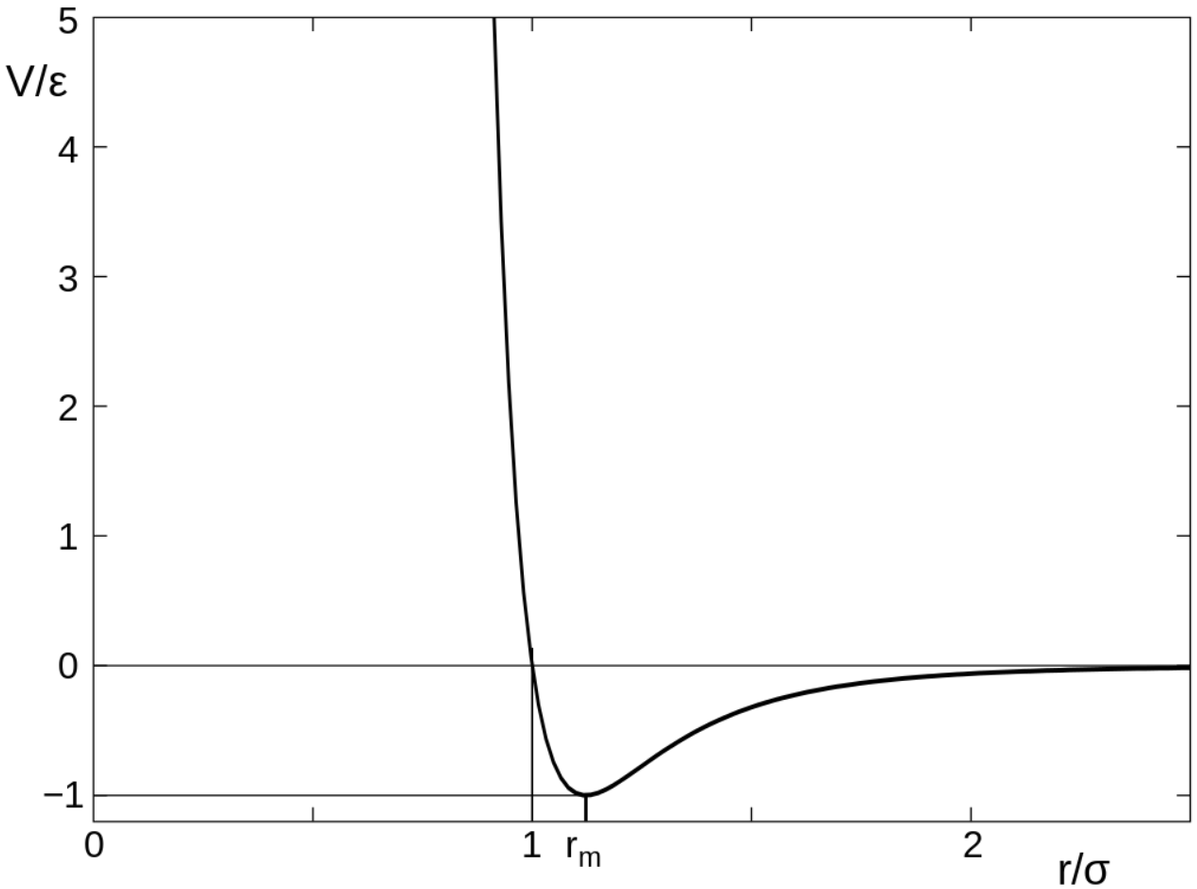
Lennard-Jones potential

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

$u^* \equiv u/\epsilon$ ↓ $r^* \equiv r/\sigma$

$$u^{*lj}(r^*) = 4 \left[\left(\frac{1}{r^*} \right)^{12} - \left(\frac{1}{r^*} \right)^{6} \right]$$



Quantity	Reduced units		Real units
temperature	$T^* = 1$	↔	$T = 119.8$ K
density	$\rho^* = 1.0$	↔	$\rho = 1680$ kg/m^3
time	$\Delta t^* = 0.005$	↔	$\Delta t = 1.09 \times 10^{-14}$ s
pressure	$P^* = 1$	↔	$P = 41.9$ MPa

Parameters for Argon

Verlet integration

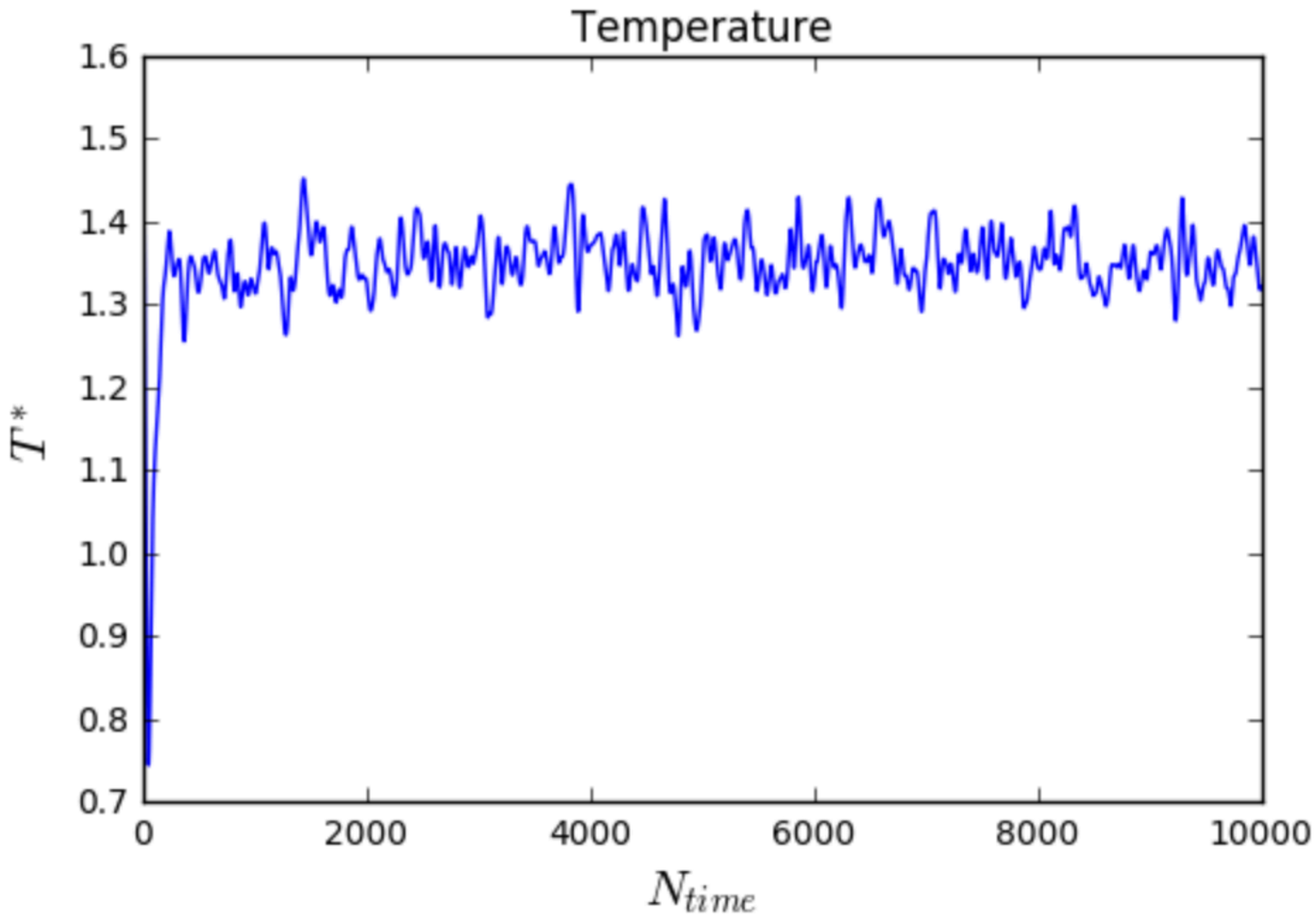
Verlet method is more numerically stable
than simpler Euler method

$$\vec{x}(t+\Delta t) = \vec{x}(t) + \vec{v}(t)\Delta t + \frac{\vec{a}(t)\Delta t^2}{2} + \frac{\vec{b}(t)\Delta t^3}{6} + O(\Delta t^4)$$

$$\vec{x}(t-\Delta t) = \vec{x}(t) - \vec{v}(t)\Delta t + \frac{\vec{a}(t)\Delta t^2}{2} - \frac{\vec{b}(t)\Delta t^3}{6} + O(\Delta t^4)$$

$$\vec{x}(t+\Delta t) = 2\vec{x}(t) - \vec{x}(t-\Delta t) + \vec{a}(t)\Delta t^2 + O(\Delta t^4)$$

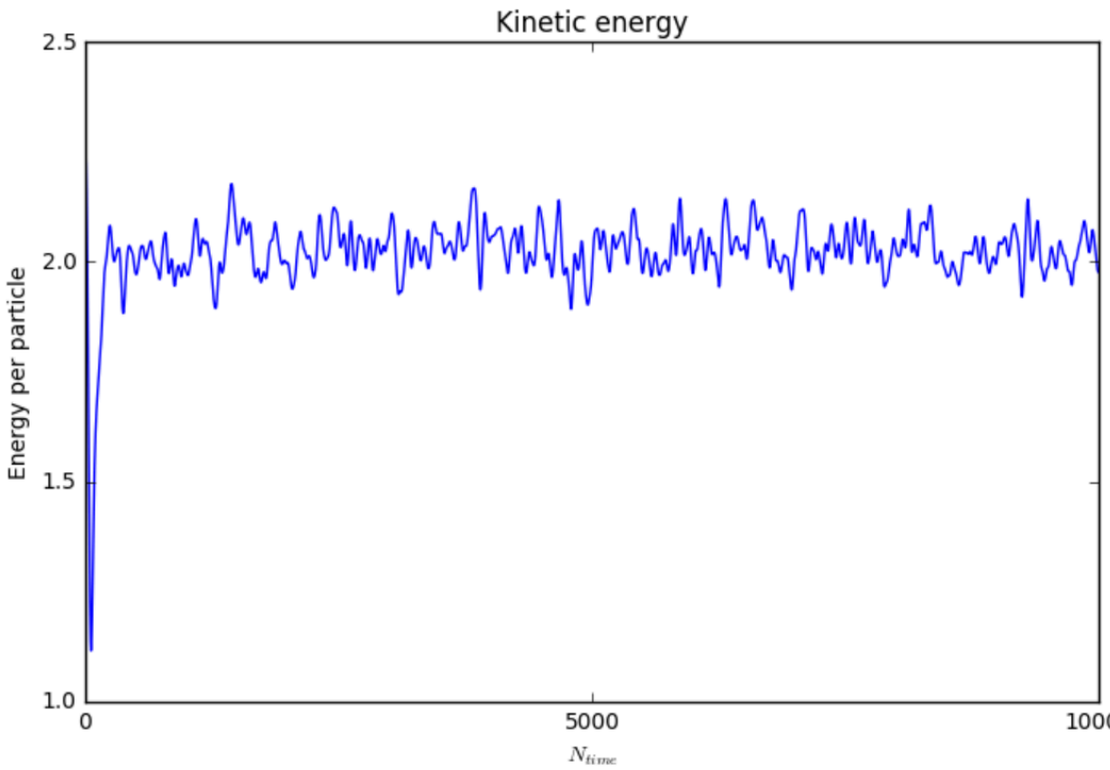
Temperature

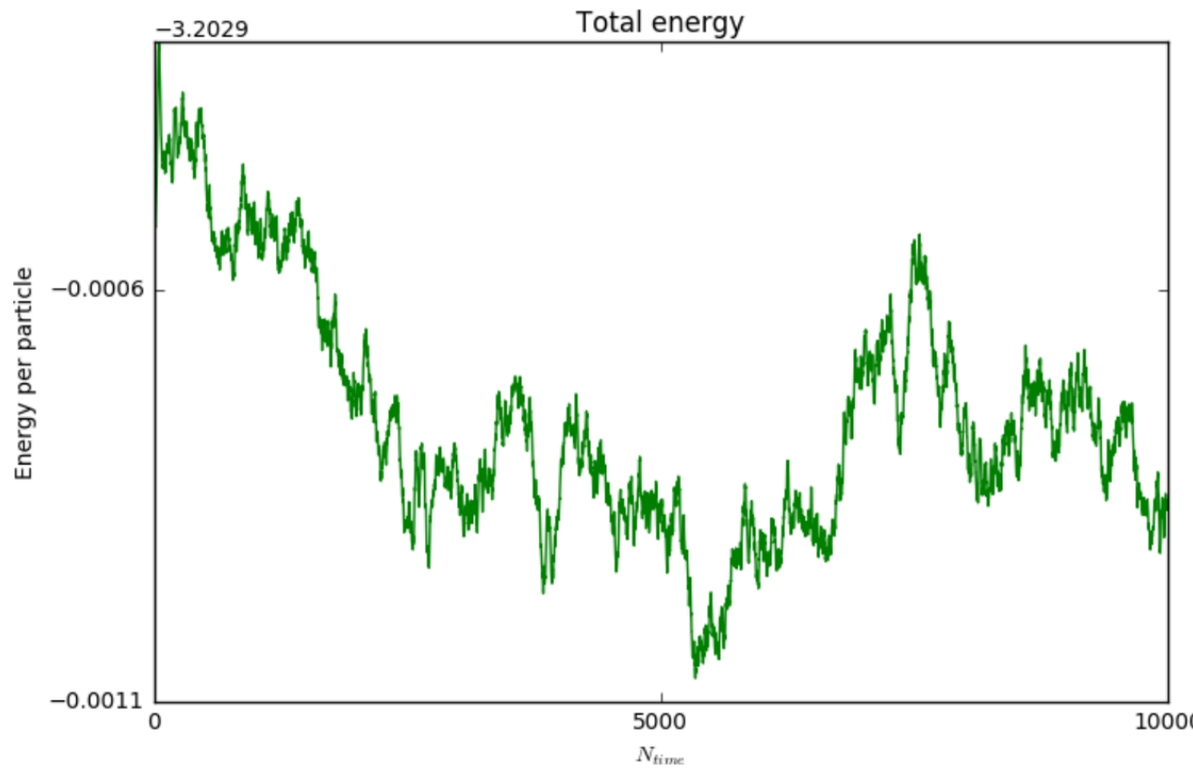


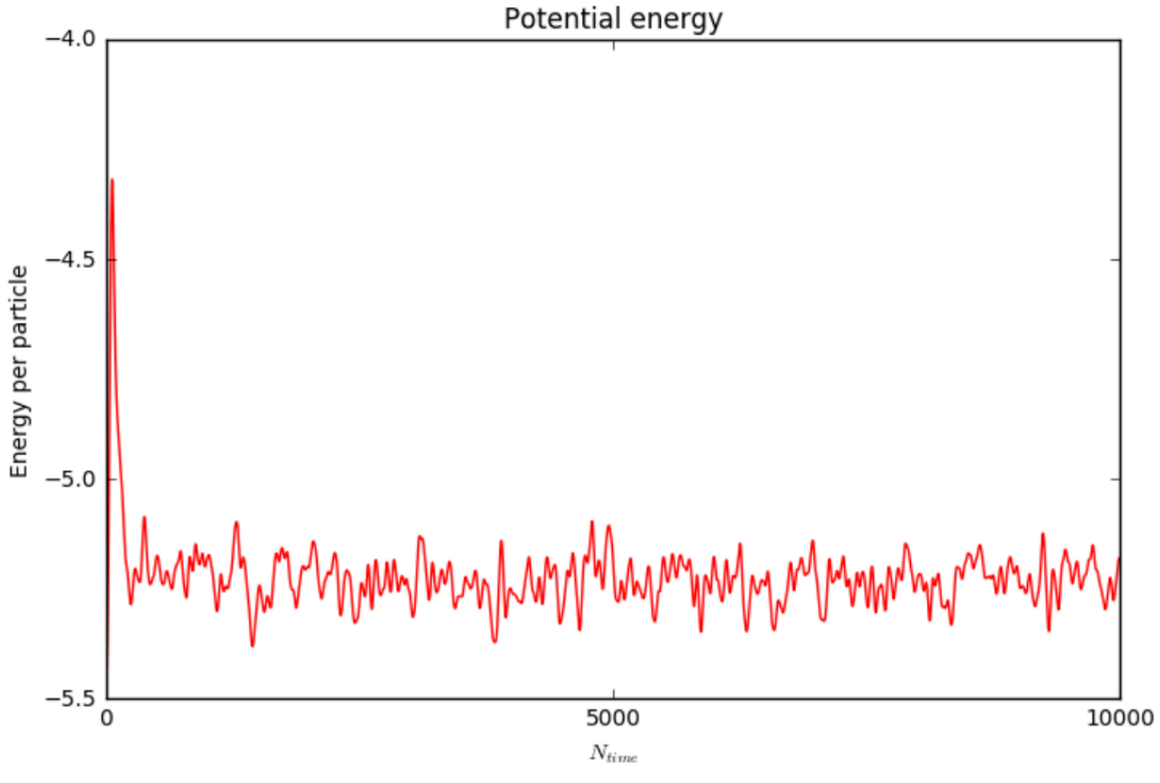
$$T(t) = \sum_{i=1}^{N} \frac{m_i v_i^2(t)}{k_B N_f}$$

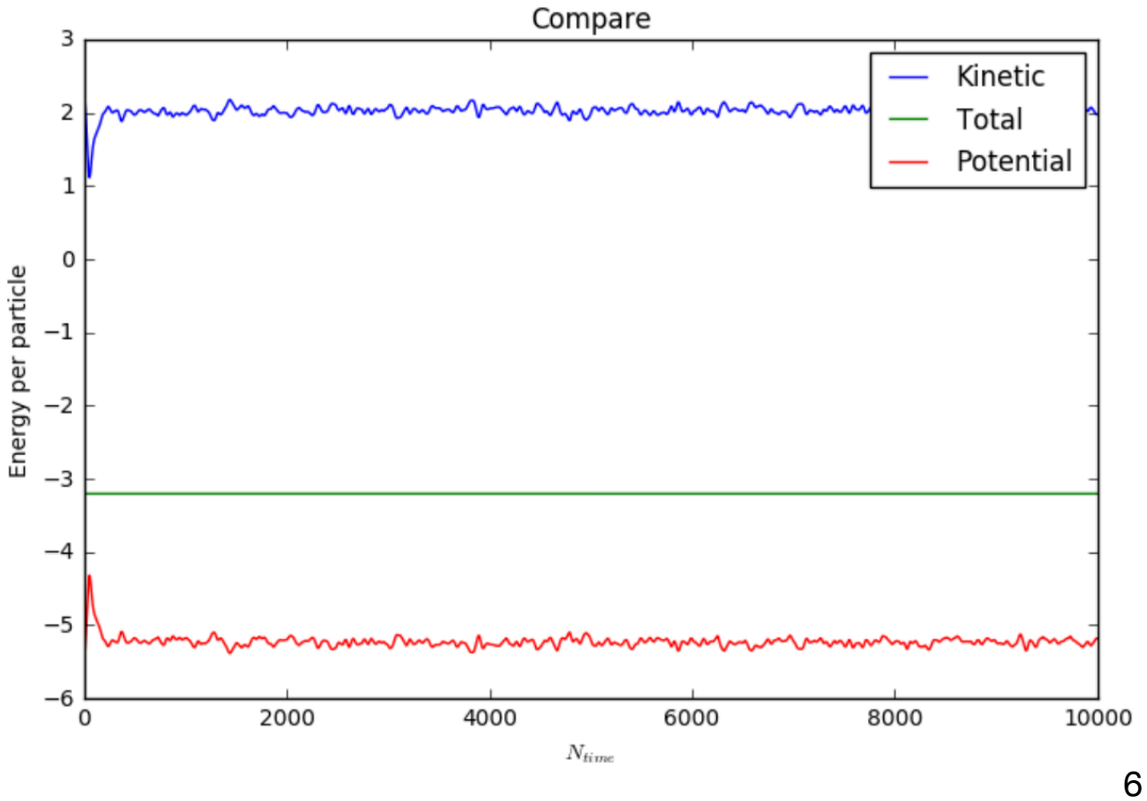
Average value: `1.3475929108`
Variance: `0.00276907131449`

Energy


Kinetic energy
Energy per particle
2.5
2.0
1.5
1.0
0
5000
10000
N_{time}

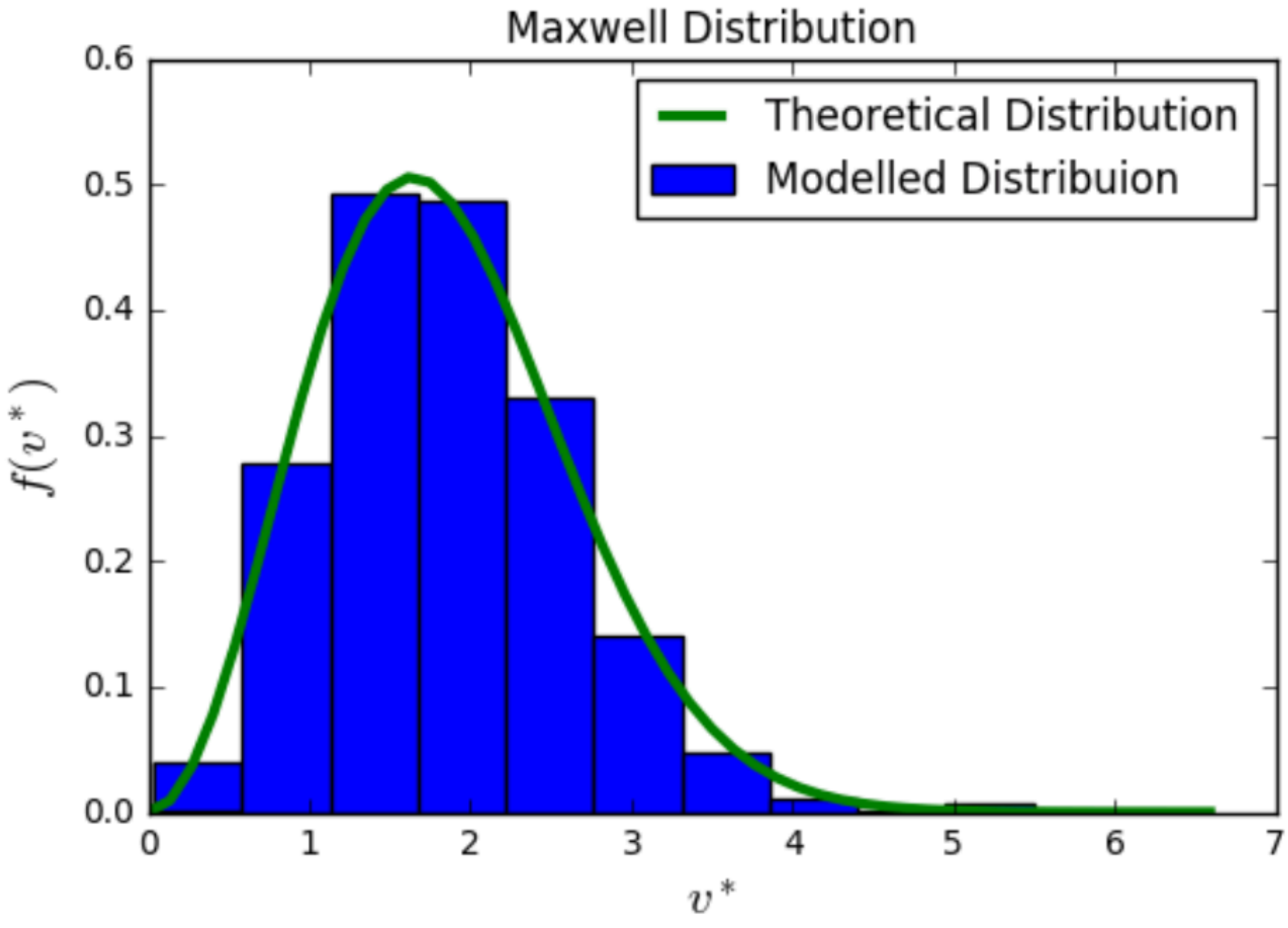

Total energy
−3.2029
−0.0006
−0.0011
Energy per particle
0
5000
10000
N_{time}


Potential energy
Energy per particle
−4.0
−4.5
−5.0
−5.5
0
5000
10000
N_{time}

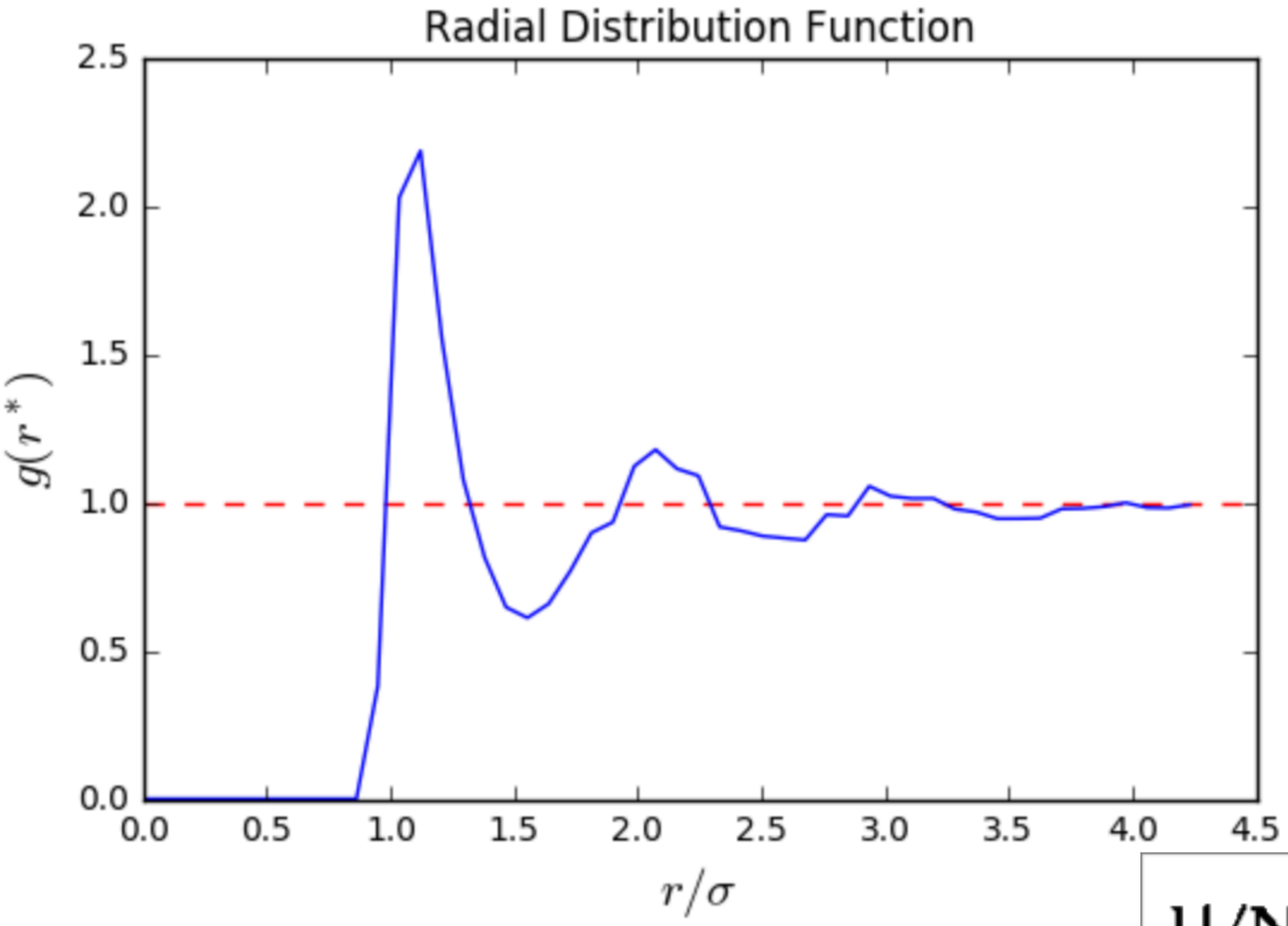

Compare
Kinetic
Total
Potential
Energy per particle
3
2
1
0
−1
−2
−3
−4
−5
−6
0
2000
4000
6000
8000
10000
N_{time}

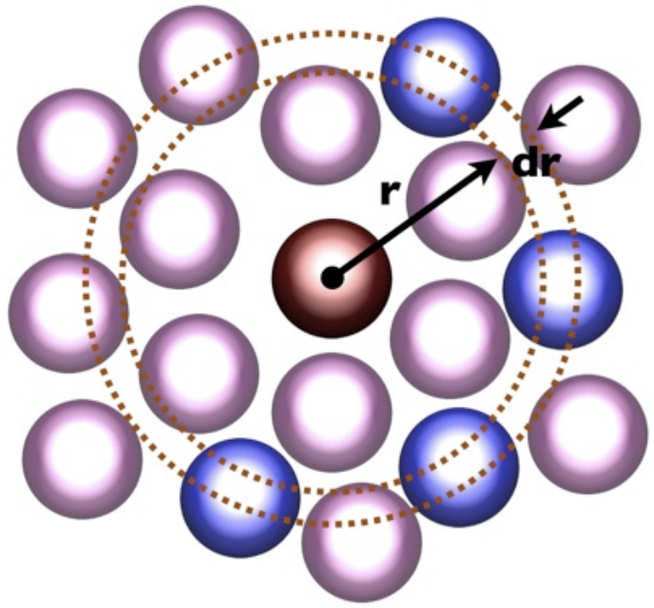
Maxwell distribution

$$f(v)dv = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{-mv^2}{2kT}\right) dv$$



Radial distribution function

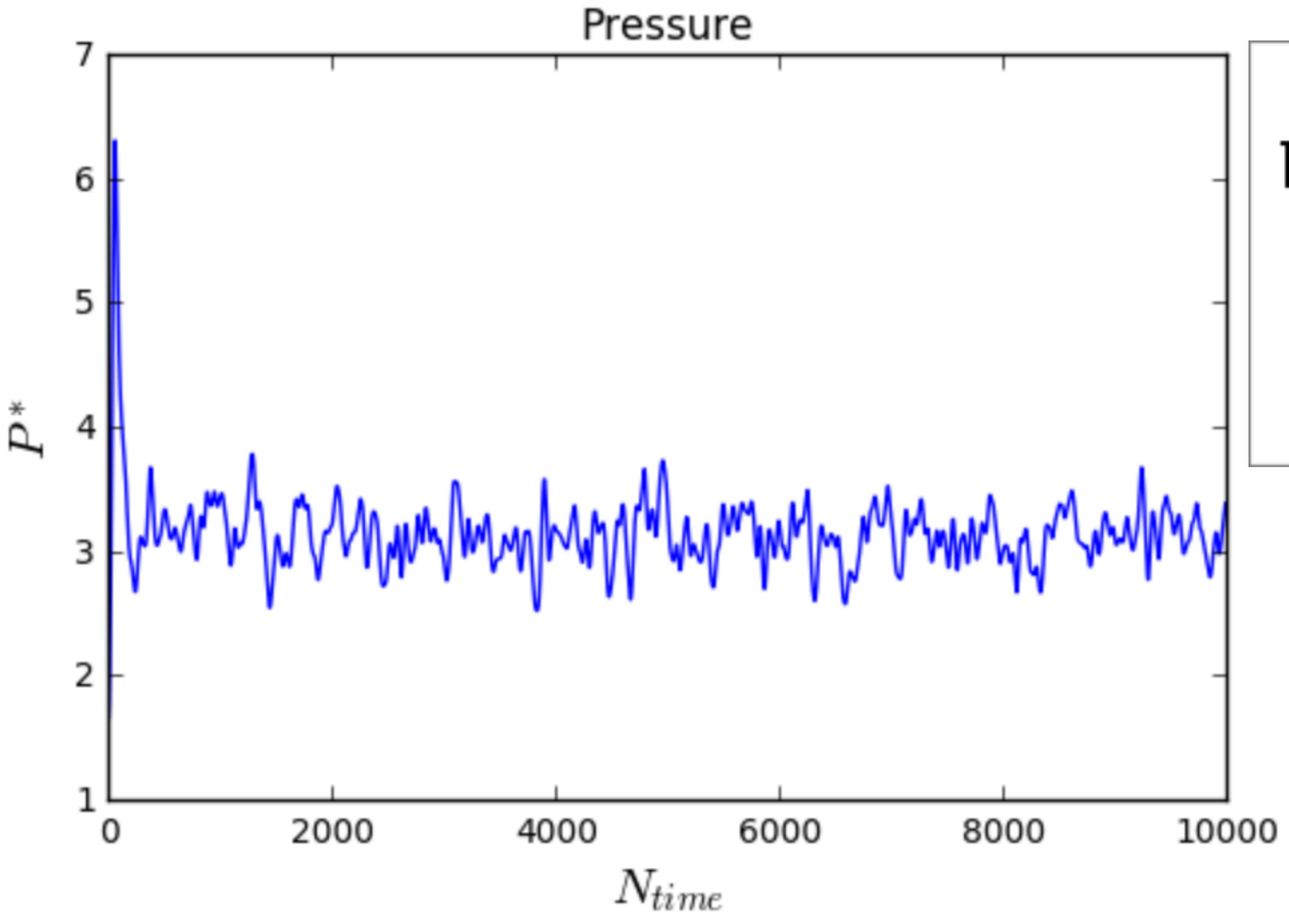




Potential energy per particle: `-5.25945299116`

$$U/N = \frac{1}{2}\rho \int_0^\infty dr\, u(r)g(r)$$
$$= 2\pi\rho \int_0^\infty dr\, r^2 u(r)g(r)$$

Calculation of the pressure



$$P = \rho k_B T - \frac{1}{3}\frac{1}{2}\rho^2 \int_0^\infty dr \, \frac{du(r)}{dr} r g(r)$$
$$= \rho k_B T - \frac{2}{3}\pi\rho^2 \int_0^\infty dr \, \frac{du(r)}{dr} r^3 g(r)$$

Density: 0.8442
Pressure: 3.0419538817

Average value: 3.1377029377
Variance: 0.0891742666069

The pressure values calculated using two methods are consistent between themselves

$$P = \rho k_B T + \frac{1}{dV}\left\langle \sum_{i<j} \mathbf{f}(r_{ij}) \cdot \mathbf{r}_{ij} \right\rangle$$

, where d is a dimensionality of system

Fluctuations

$$\frac{\sqrt{\overline{\Delta F^2}}}{\overline{F}} = \frac{1}{N^{1/2}} \frac{\sqrt{\overline{\Delta f^2}}}{\overline{f}} \sim N^{-1/2}$$

Relative fluctuations decrease with an increase in the number of particles in the system and is very small when N is huge

$$\delta F = \pm\sqrt{\overline{(F-\overline{F})^2}} = \pm\sqrt{\overline{(\Delta F)^2}}$$

Mean squared fluctuations

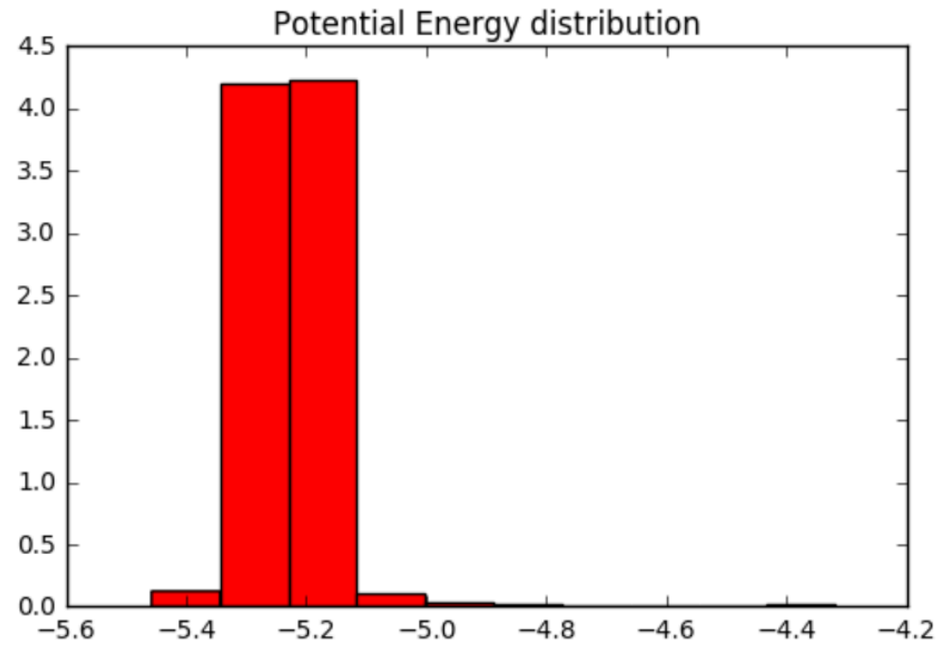
$$\delta F/\overline{F}$$

Relative mean squared fluctuations

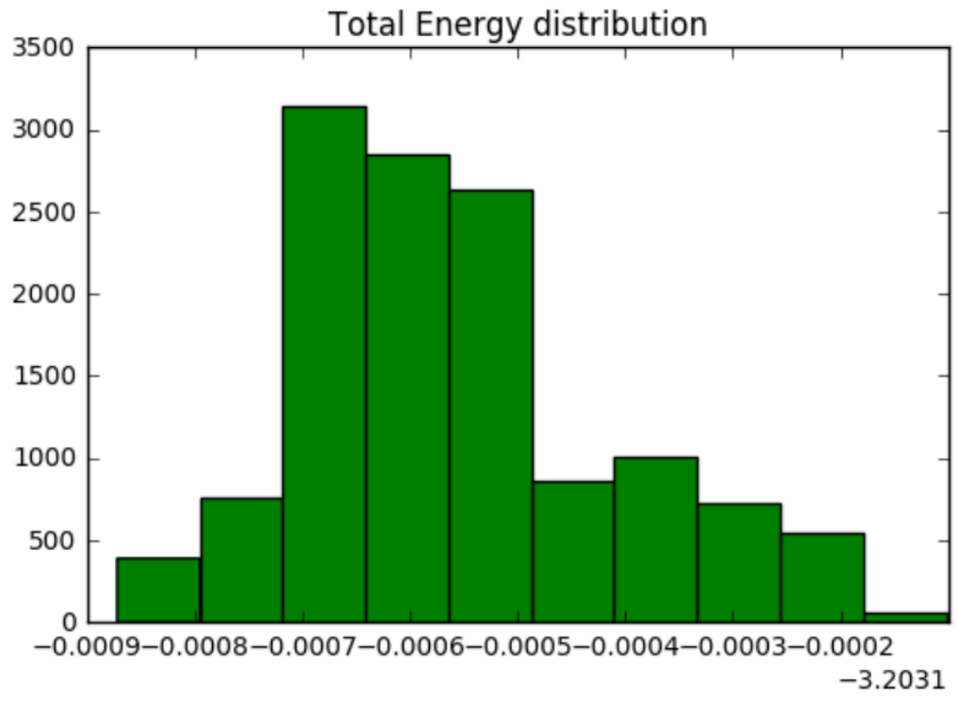
$$W = \frac{1}{\sqrt{2\pi\overline{\left(F-\overline{F}\right)^2}}} \cdot \exp\left(-\frac{(F-\overline{F})^2}{2\overline{(F-\overline{F})^2}}\right)$$

In equilibrium systems the random variable F is often distributed around its average according to normal law

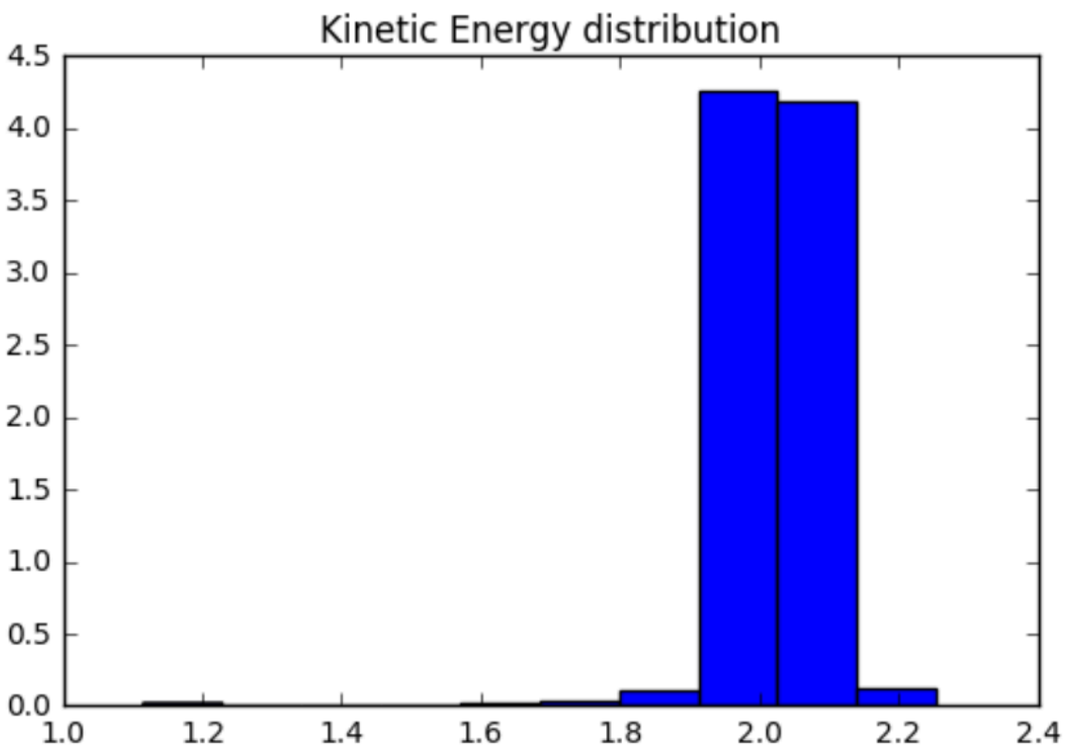
Fluctuations



Average value: `-5.225047142`
Relative mean squared fluctuation: `0.0151151942524`



Average value: `-3.203657781`
Relative mean squared fluctuation: `4.56483135623e-05`



Average value: `2.021389367`
Relative mean squared fluctuation: `0.0390488606655`

The value is obtained using radial distribution function

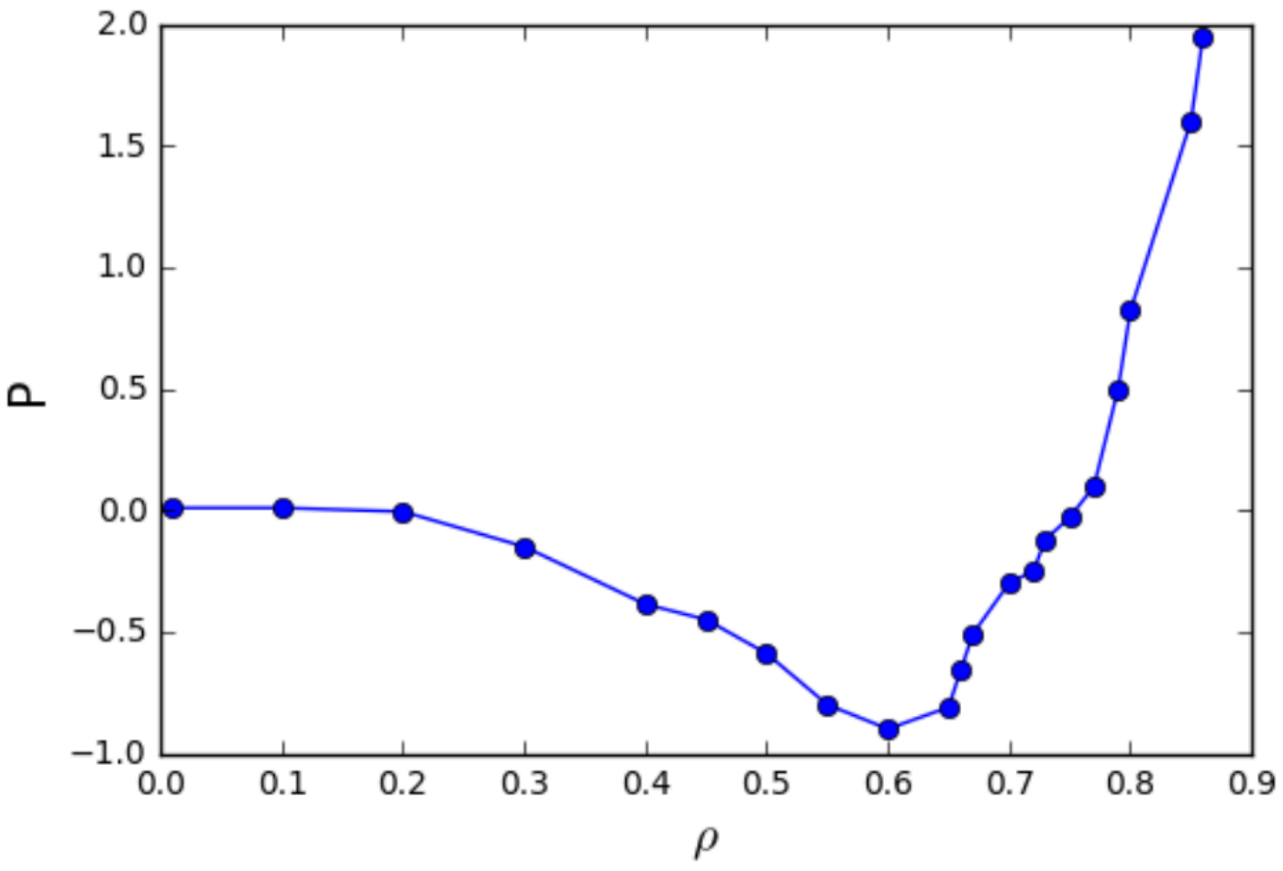
Potential energy per particle: `5.25945299116`

This agrees with average potential energy obtained experimentally

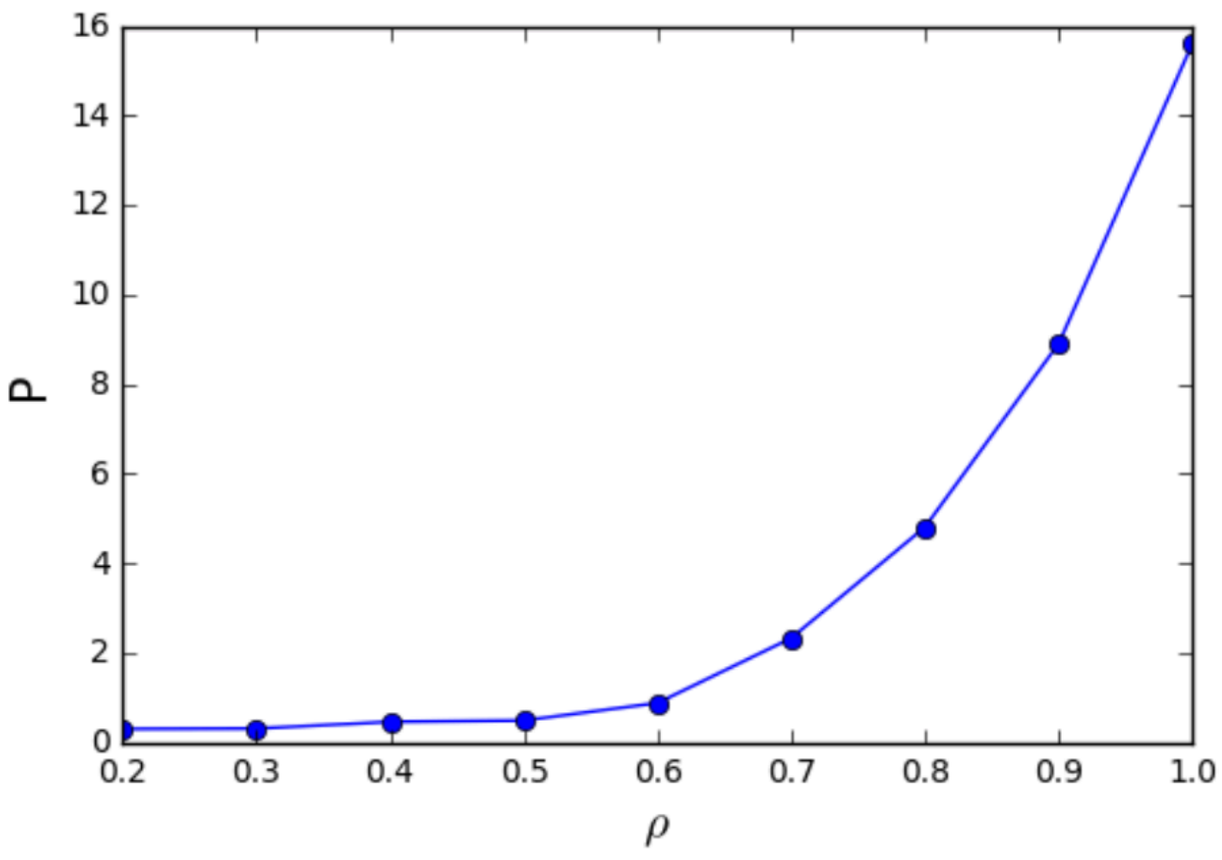
Equation of state for the Lennard-Jonesfluid

125 atoms

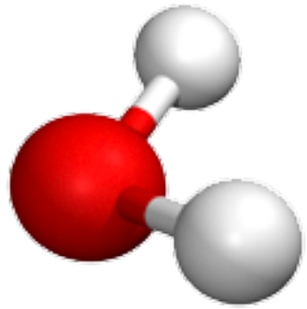
Isothermal curve with temperature under critical point: T=0.9



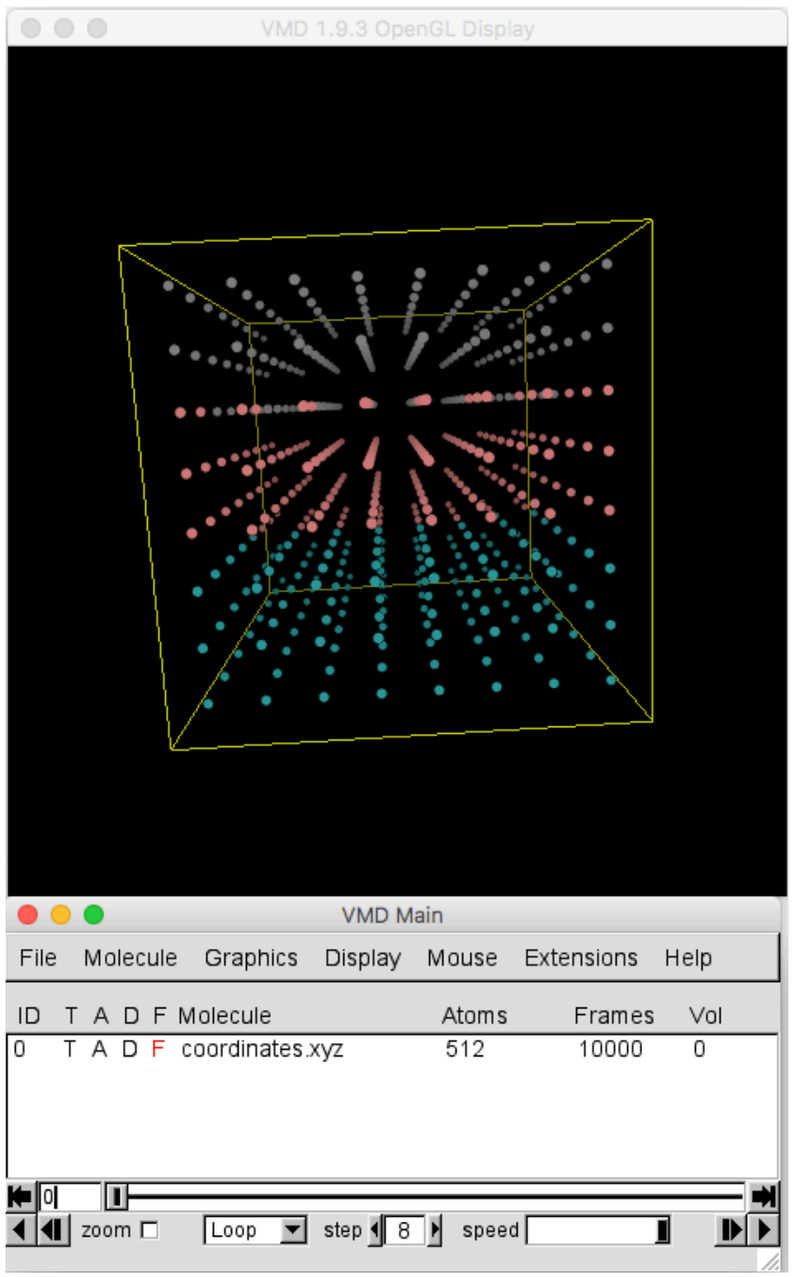
Isothermal curve with temperature T=2.0



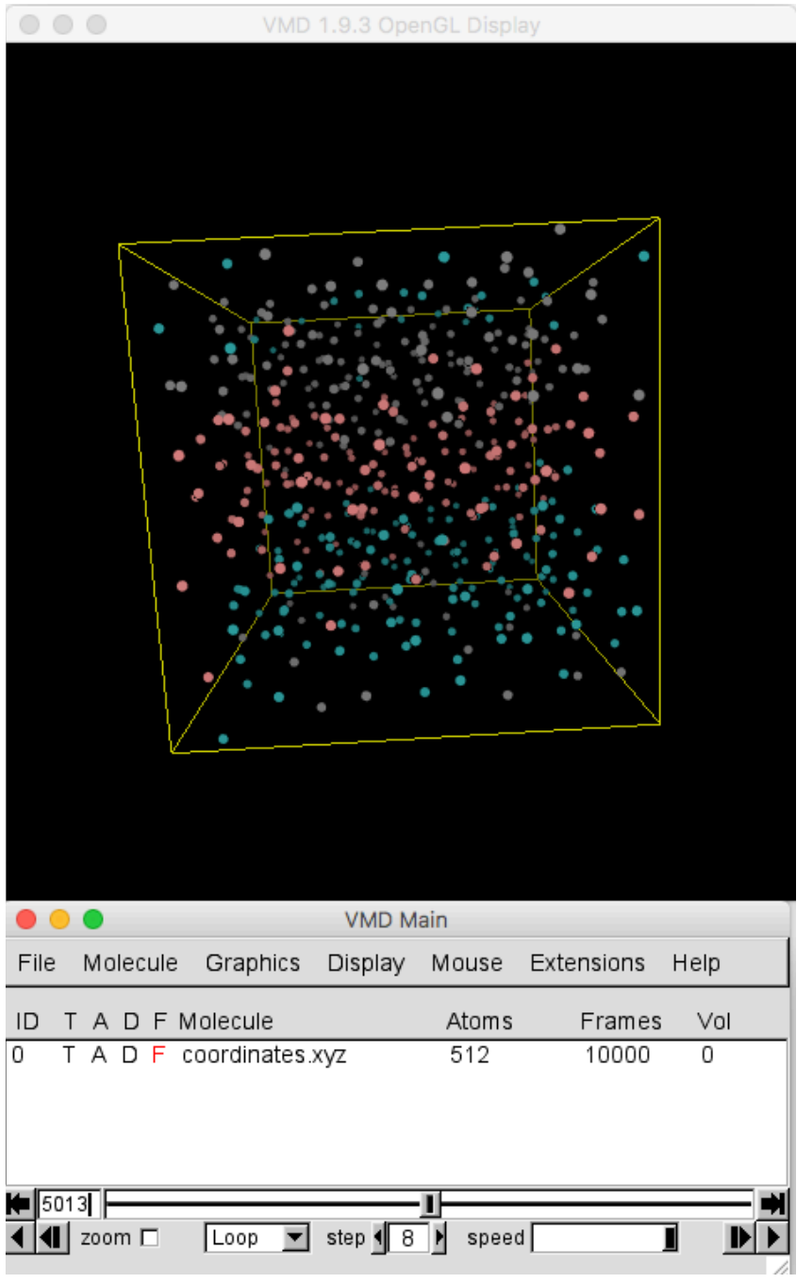
Visual Molecular Dynamics (VMD)



512 atoms



0/10000



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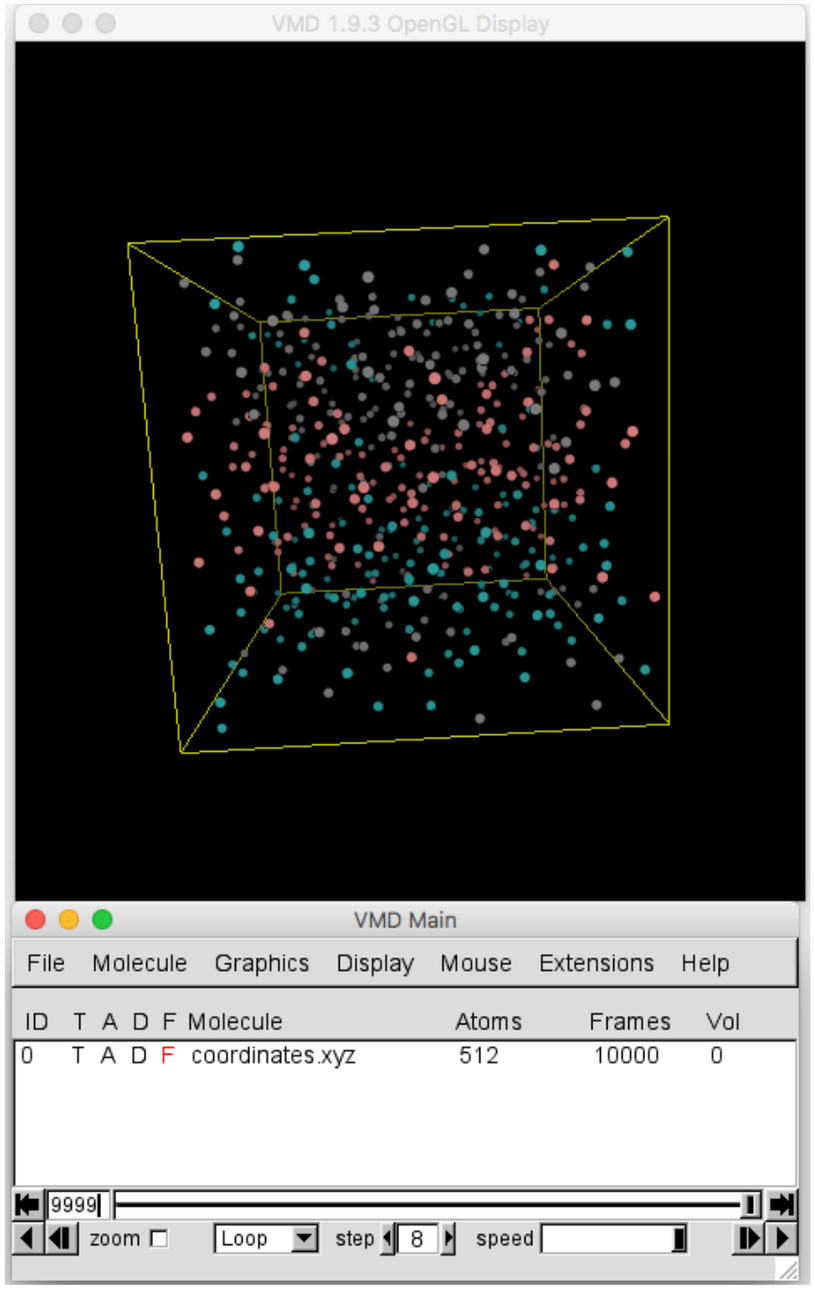

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References

- *Прут Э.В., Кленов С.В., Овсянникова О.Б.* Элементы теории флуктуаций и броуновского движения в молекулярной физике - М.: МФТИ, 2002.

- *Frenkel D., Smit B.* Understanding Molecular Simulation. From Algorithms to Applications - Academic Press, 2002.

- Molecular Dynamics - program written in C using OpenMP framework for parallel computing. Used VMD for visualization. Code on GitHub - https://github.com/akarazeev/MolecularDynamics-3sem-MIPT-2015