Laboratory of Computational Physics

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Table of contents

1 Soft-Core Molecular Dynamics in 3*d*

We now consider a system of N particles enclosed in a box with PBC and interacting through a smooth central potential which is repulsive at short range and attractive at large distances. The most common form of this kind of potential is the **Lennard-Jones** (L-J) potential:

$$U(r) = 4\,\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \qquad r = |\vec{x}| \tag{1}$$

where ε is the depth of the potential well, σ is the finite distance at which the inter-particle potential is zero and r is the distance between the particles. Upon differentiation we obtain the force acting between pair of particles:

$$F(r) = -\frac{\partial}{\partial r}U(r) = 24\,\frac{\varepsilon}{\sigma}\left[2\left(\frac{\sigma}{r}\right)^{13} - \left(\frac{\sigma}{r}\right)^{7}\right] \tag{2}$$

To save computational time and satisfy the minimum image convention, the Lennard-Jones potential is often truncated at a cut-off distance of $r_c = 2.5\,\sigma$, where:

$$U(r_c) = 4\,\varepsilon\left[\left(\frac{1}{2.5}\right)^{12} - \left(\frac{1}{2.5}\right)^{6}\right] \approx -0.0163\,\varepsilon \tag{3}$$

At distances larger than r_c the potential is less than $\frac{1}{60}$ the minimum value ε, therefore the truncation gives us a good approximation of the full potential. As a consistency measure, we assume $r_c < L$, with L being the size of the box ($L^d = V$).

Since the truncation introduces a jump discontinuity at the cut-off distance, we need to shift the potential upward so that $U(r_c) = 0$ and also impose that the first derivative is continuous in the interval $(0,\infty)$. The truncated and shifted potential is defined as follows:

$$U_{\text{trunc}}(r)=\begin{cases} U(r)-U(r_c)+(r-r_c)\,F(r_c) & \text{for} \quad r\leq r_c \\ 0 & \text{for} \quad r>r_c \end{cases} \tag{4}$$

where $F(r_c)$ is the value of the force at the cut-off:

$$F(r_c)=24\,\frac{\varepsilon}{\sigma}\left[\left(\frac{1}{2.5}\right)^{13}-\left(\frac{1}{2.5}\right)^{7}\right]\approx-0.039\,\frac{\varepsilon}{\sigma} \tag{5}$$

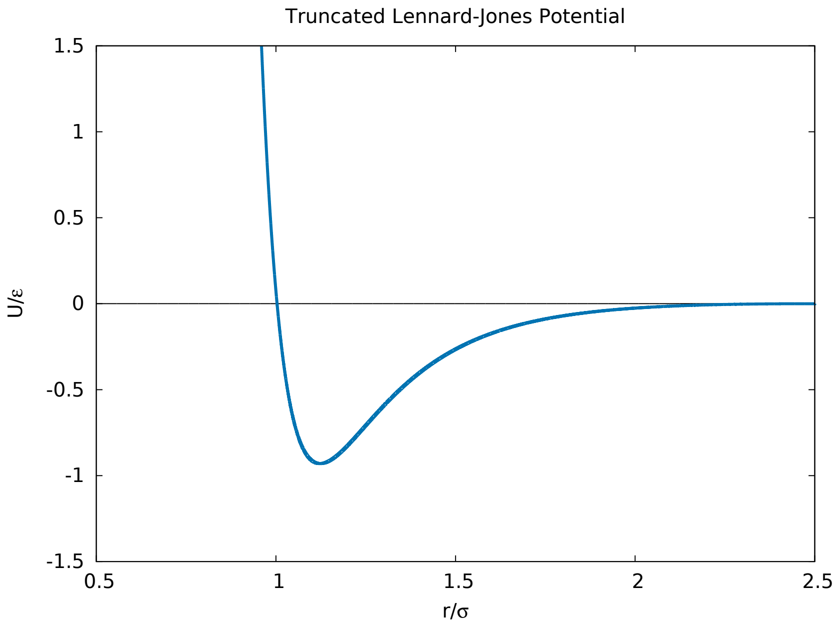


Figure 1. Plot of the truncated L-J potential.

Since the L-J potential depends only upon the two parameters σ and ε, which determine the length and energy scales of the system, we can choose to work in adimensional units where:

$$m=1, \quad \sigma=1, \quad \varepsilon=1, \quad L\neq 1 \tag{6}$$

The time evolution of the system is obtained by numerical integration of the equations of motion. The method employed is the **Velocity Verlet** algorithm, which consists of the four steps:

1. half step velocity update: $\vec{v}\left(t+\frac{1}{2}\Delta t\right)=\vec{v}(t)+\frac{1}{2}\,\vec{a}\,(t)\,\Delta t$

2. full step position update: $\vec{x}\,(t+\Delta t)=\vec{x}\,(t)+\vec{v}\left(t+\frac{1}{2}\Delta t\right)\Delta t$

3. recompute accelerations: $\vec{a}\,(t+\Delta t)=\frac{1}{m}\,\vec{F}(t+\Delta t)$

4. half step velocity update: $\vec{v}\,(t+\Delta t)=\vec{v}\left(t+\frac{1}{2}\Delta t\right)+\frac{1}{2}\,\vec{a}\,(t+\Delta t)$

where in step (2) we must apply periodic boundary conditions in each of the d directions. The unit time interval is chosen to be $\Delta t=0.001$.

For conservative systems, it can be shown that the energy of the Verlet approximation essentially oscillates around the constant energy of the exactly solved system, with a global error bound of order $\mathcal{O}(\Delta t^2)$.

Technical Note: in order to further reduce the computational cost of the algorithm, we construct a table T_{ij} in which we save, for each particle i, the list of neighbouring particles j at distances $r_{ij} < 2.8\ \sigma = r_m$. Only the particles inside the neighbour list are taken into account in the calculations of the accelerations. The list itself is then updated once every 10 evolution steps to keep up with the movement of the particles.

1.1 Thermalization

Particles are initialized in a regular BCC lattice structure with momenta randomly assigned in the multi interval $[-1,1]^d$. The istantaneous temperature $k\,T = \frac{2}{d}K$ can then be set to a desired value $k\,T'$ by rescaling the momenta as:

$$p_i \rightarrow p_i' = p_i\sqrt{\frac{k\,T'}{k\,T}} \tag{7}$$

While the mechanical energy $H = K + U$ is conserved in time, the kinetic energy K and the temperature $k\,T$ are not, hence the rescaling of (7) must be repeated at regular intervals until thermalization is reached.

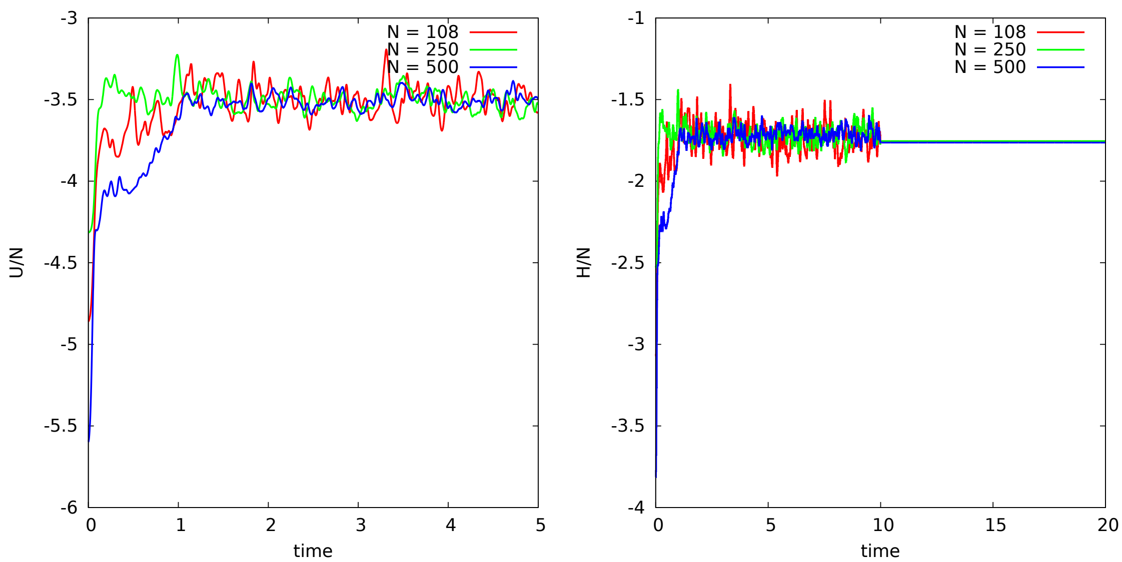


Figure 2. Thermalization of a system of softcore particles at density $\rho = 0.7$, $k\,T = 1.19$ for $N = 108, 250, 500$. On the left we show the evolution of the density of potential energy $U\,/\,N$ in the first 5000 integration steps. On the right is the total energy density $H\,/\,N$, first during the thermalization phase $(0 < t < 10)$, in which the temperature is kept constant, and then in the measurement phase $(t > 10)$ when the energy H is constant.

We define the *density* of the system as:

$$\rho = \frac{N\sigma^d}{L^d} \quad \Longrightarrow \quad L = \sigma\left(\frac{N}{\rho}\right)^{\frac{1}{d}} \tag{8}$$

and, since $\sigma = 1$, we can choose to define the properties of the system by setting some values for N and ρ, thus automatically fixing the value of L.

1.2 Momentum Distribution

Because the system in exam is not an ideal gas, the probability distribution of the momenta could in principle be quite different from the Maxwell-Boltzmann distribution. However, the L-J potential is still a good approximation of that of an ideal gas expecially at low densities where the gas is very rarefied.

In (Fig.3) we show that a gas of $N = 250$ particles at $\rho = 0.5$ and $k\,T = 1$, reaches thermal equilibrium with a Maxwell Boltzmann distribution:

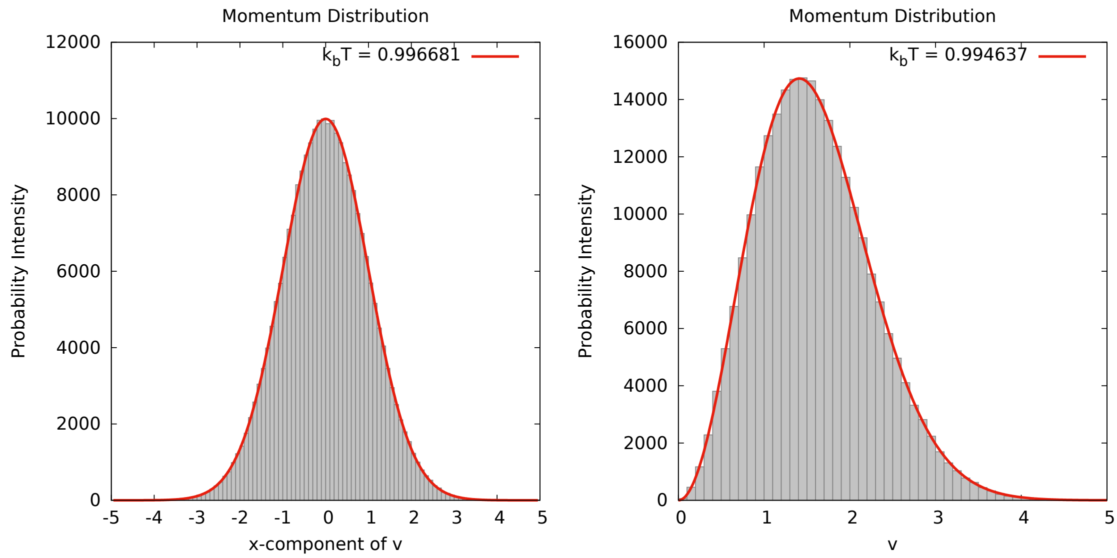


Figure 3. Momentum distributions for a system of $N = 250$ particles at $\rho = 0.5$ and $k_b T = 1.0$. On the left is the v_x distribution and on the right is the distribution of the modulus of the momentum. The measurements were taken every 100 evolution steps for 10^5 steps, each time collecting the momenta of every particle thus giving a total of 250000 samples. The simulation was preceded by a thermalization phase of $t_{\text{therm}} = 5000\,\Delta t = 5$. The red lines represent fits with Maxwell-Boltzmann distributions.

We can compare the initial temperature of the simulation with the widths of the distributions to establish if the system has reached equilibrium at the right temperature. The results of the fit are in fact in good accordance with the chosen value $k\,T = 1.0$:

$$\begin{aligned} k\,T &= 0.997 \pm 0.003 \quad (v_x \text{ fit}) \\ k\,T &= 0.995 \pm 0.002 \quad (|\vec{v}| \text{ fit}) \end{aligned}$$

1.3 Potential Energy and Fluctuations

We define the density of potential (internal) energy:

$$u = \frac{U}{N} \tag{9}$$

as the average potential energy associated to each particle, and study its fluctuations around the mean value $\langle u \rangle$, since, as pointed out before, the quantities K and U are not conserved individually but only as the sum $H = K + U$.

We compute the time evolution of the observable u for systems of $N = 108, 250, 500$ particles at density $\rho = 0.7$ and initial temperature $kT = 1.19$.

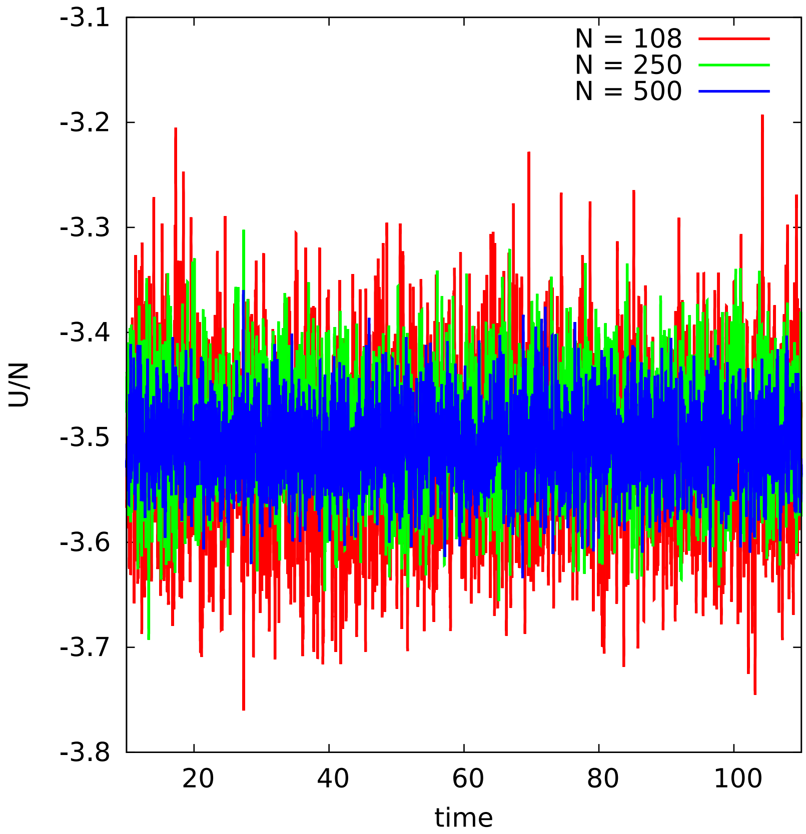


Figure 4. Internal energy density u for $N = 108, 250, 500$ at $\rho = 0.7$ and $kT = 1.19$. Thermalization time $t_{\text{term}} = 10$ and total time of the simulation $t = 100$ ($\Delta t = 0.001$). During the thermalization phase the momenta were rescaled every 10 steps in order to fix the temperature to the desired value.

N	$\langle u \rangle$	Δu
108	-3.5141	0.0760
250	-3.4948	0.0501
500	-3.5066	0.0358

These results were obtained by averaging over a set of 10^3 measurements taken once every 100 evolution steps in order to reduce autocorrelation effects. The measurement phase was also preceded by a thermalization time $t_{\text{therm}} = 10$.

We immediately notice that the amplitude of the fluctuations decreases as the number of particle N gets larger. In fact, for a macroscopic system, we expect both the variance and the mean of the energy to scale as N, hence:

$$\frac{\Delta U^2}{\langle U \rangle^2} = \frac{\langle U^2 \rangle - \langle U \rangle^2}{\langle U \rangle^2} \sim \frac{1}{N} \xrightarrow[N \to \infty]{} 0 \tag{10}$$

As a consequence, if we consider the density u, we have:

$$u = \frac{U}{N} \sim \frac{N}{N} = 1, \qquad \Delta u = \sqrt{\langle (u - \langle u \rangle)^2 \rangle} = \frac{\Delta U}{N} \sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}} \xrightarrow[N \to \infty]{} 0 \tag{11}$$

which implies:

$$\Delta u \cdot \sqrt{N} \sim \text{const.} \qquad \begin{cases} 0.0760 \cdot \sqrt{108} & \approx & 0.789815... \\ 0.0501 \cdot \sqrt{250} & \approx & 0.792151... \\ 0.0358 \cdot \sqrt{500} & \approx & 0.800512... \end{cases}$$

This is actually the well known result that, in the thermodynamic limit, the energy of a grand-canonical ensamble converges to its expectation value, thus giving a physically equivalent description to that of a micro-canonical ensamble.

1.4 Energy, Temperature and Pressure

Another quantity of interest for a soft-core interecting gas is the pressure, defined using the **virial theorem**:

$$\frac{PV}{NkT} = \frac{P\sigma^3}{\rho kT} = 1 + \frac{1}{d\,NkT} \sum_{i<j} \langle \vec{r}_{ij} \cdot \vec{F}_{ii} \rangle \tag{12}$$

where the sum ranges over all the pairs of particles and $\langle\ \rangle$ represents the time average. If the system had the properties of an ideal gas, then the previous formula would yield zero because there would not be any interaction between particles. In the case of a L-J potential we can use the measurement of the pressure as an indicator of the deviation from the ideal gas behavior.

In this section we consider a system of $N = 108$ particles at $\rho = 0.6$ and temperature $kT = 1.22$. We simulate for a total time $t = 110$ with $\Delta t = 0.001$ and with the first 10^4 timesteps ($t = 10$) dedicated to the thermalization of the system during which the temperature is reset every 10 steps.

The averages and standard deviations on the observables are computed with data collected every 100 steps, in order to reduce autocorrelation effects.

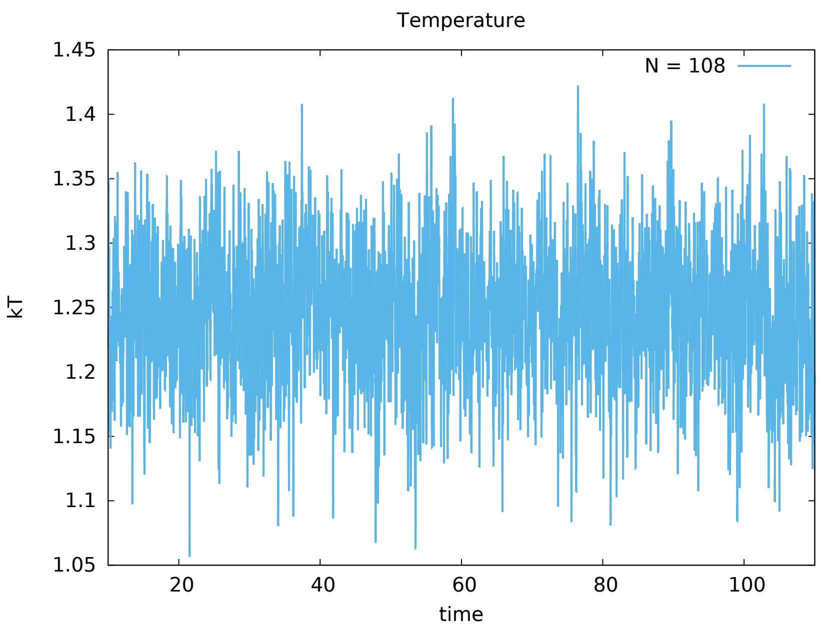


Figure 5. Temperature as a function of time for $N = 108$, $\rho = 0.6$ and initial temperature $kT = 1.22$.

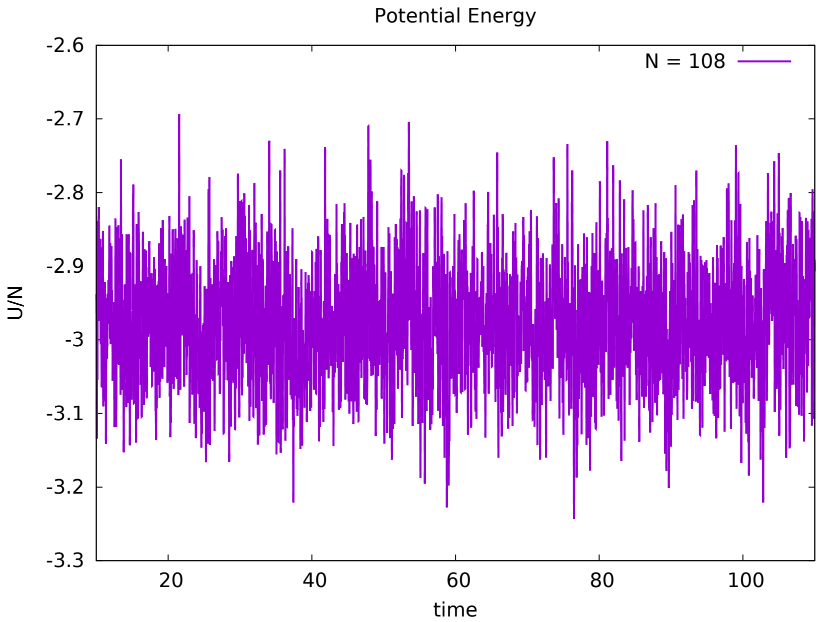


Figure 6. Potential energy as a function of time for $N = 108$, $\rho = 0.6$ and initial temperature $kT = 1.22$.

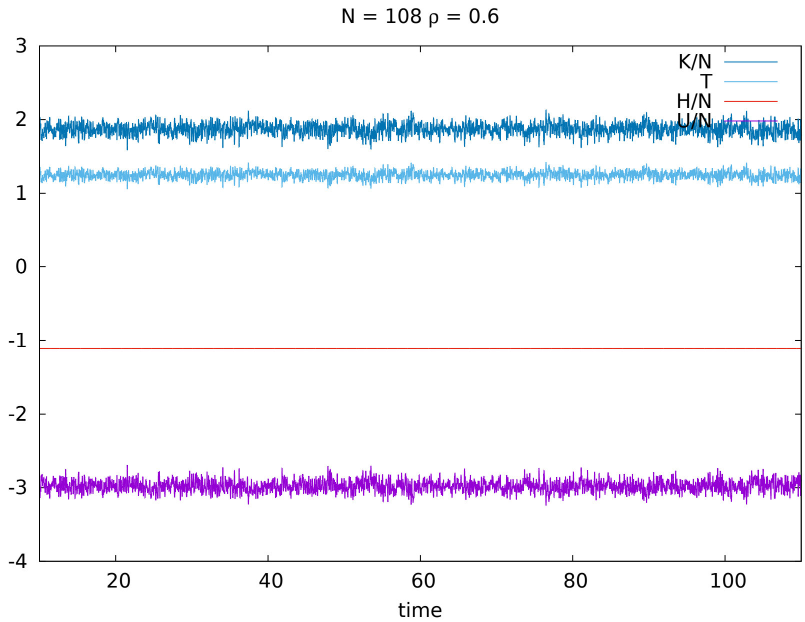


Figure 7. We plot, from the top, the kinetic energy $\frac{K}{N}$, the instantaneous temperature kT, the mechanical energy $\frac{H}{N}$ and the potential energy $\frac{U}{N}$ for $N = 108$, $\rho = 0.6$ and initial temperature 1.22.

We note that, because of the approximate conservation of the mechanical energy, the potential energy U and the kinetic energy K have opposite fluctuations around their respective expectation values. On the other hand the temperature T is simply proportional to K and therefore its fluctuations are proportional to those of the kinetic energy.

$$\langle u \rangle = -2.979756, \qquad \sigma_{\mathrm{std}}(u) = 0.075043 \tag{13}$$

$$\langle kT \rangle = 1.247323 \qquad \sigma_{\mathrm{std}}(kT) = 0.050026 \tag{14}$$

Finally we measure the pressure:

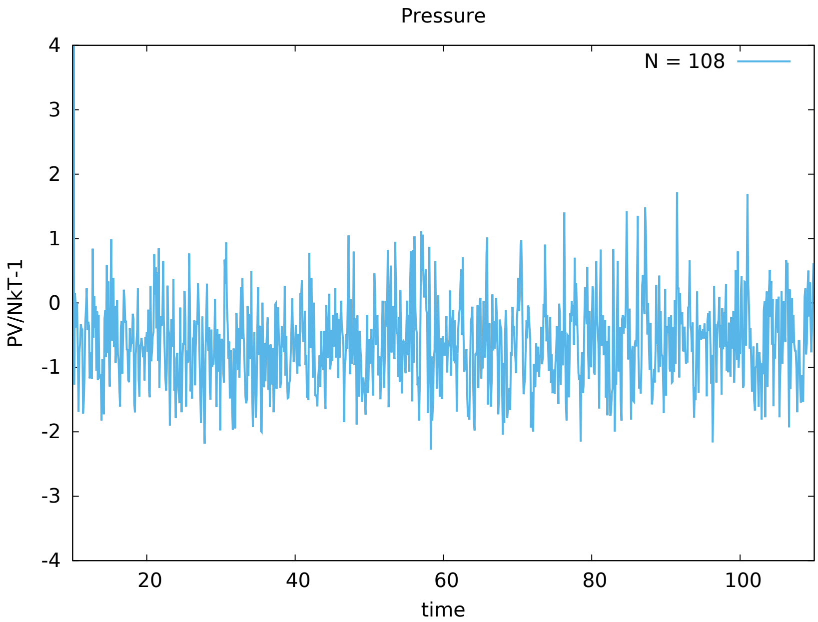


Figure 8. Pressure as a function of time for $N=108$, $\rho=0.6$ and initial temperature $kT=1.22$.

$$\frac{PV}{NkT}-1=-0.609228\pm0.029351 \tag{15}$$

As we can see from (Fig.8), the average pressure value is very close to zero, which is what we expect being the L-J gas a good approximation of an ideal gas.

1.5 Mean Squared Displacement

The computation of the MSD is done in the same way as for the case of the hard-core gas in $3d$. The system taken in consideration is a L-J gas of $N=250$ particles at $\rho=0.9$ first at initial temperature $kT=0.8$ and then at $kT=1.087$:

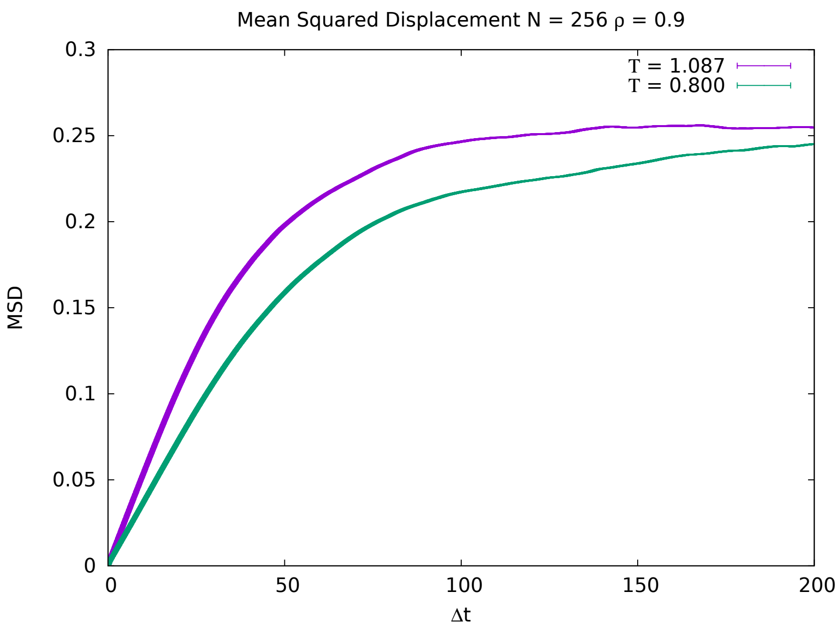


Figure 9. MSD for a system with $N=250$, $\rho=0.9$ at temperatures $kT=0.8, 1.087$. The measurements were taken every 100 evolution steps for a total time of $t=300$ after a thermalization phase of $t_{\text{them}}=10$. The points with $\Delta t>200$ are discarded because of the lower statistics.

Both systems display an initial diffusive behavior given by the typical linear form of the MSD of diffusive processes, but for higher time intervals they converge to the constant value $1/4$ because of the finite size of the system and of the PBC. The rate of diffusion decreases as the temperature is lowered until the system undergoes a liquid-solid phase transition.

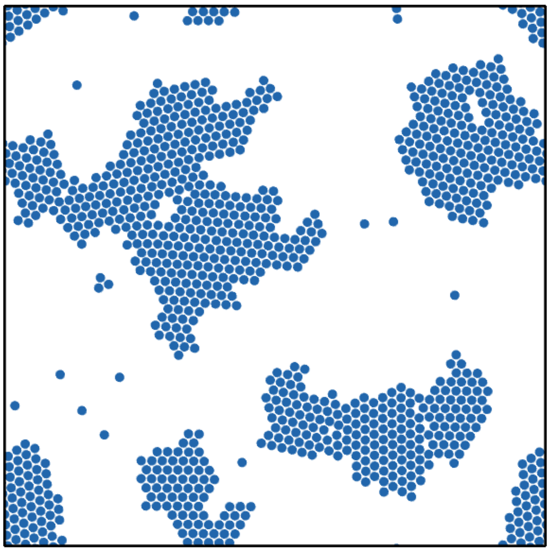


Figure 10. Example of solidification of a $2d$ L-J system of 1000 particles at $\rho = 0.3$ at $kT = 0.1$. Because of the cut-off in the potential, the solid regions do not interact with each other. Each of those regions act as an isolated system.

1.6 Thermodynamic Limit

Finally we study the thermodynamic limit extrapolation of the temperature and of the potential energy for systems at fixed density $\rho = 0.7$ and varying number of particles N[1]. We also fix the mechanical energy to the value $H/N = -2.98$ and express every quantity in terms of the parameter $1/N$.

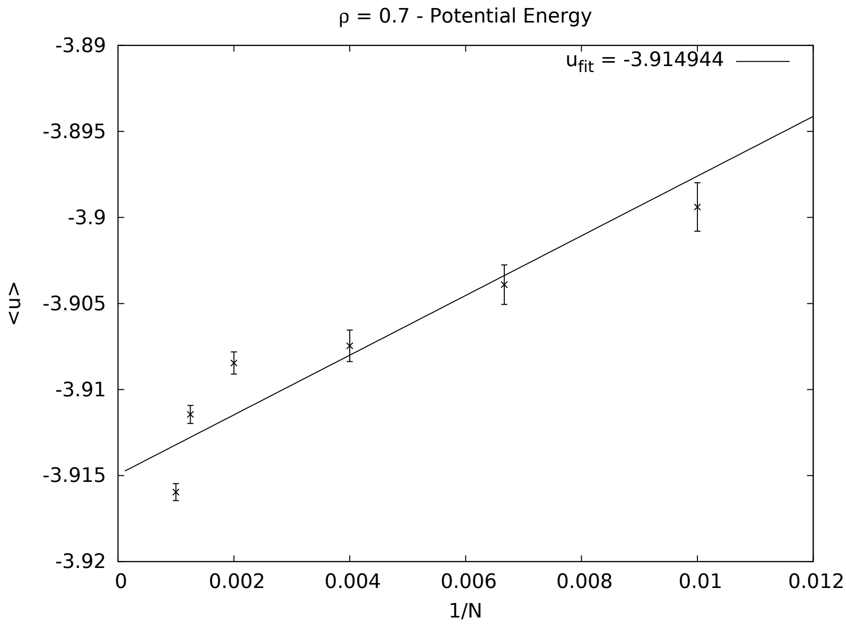
We assume that for large N, both the temperature and the potential energy have a linear functional form in the variable $1/N$:

$$u = u_\infty + m \cdot \frac{1}{N} \tag{16}$$

$$T = T_\infty + m \cdot \frac{1}{N} \tag{17}$$

so that by fitting the data obtained at different N we can extrapolate the thermodynamic limit of those observables.

1. The thermodynamic limit consists, in fact, in sending N and $V = L^d$ to infinity while keeping the ratio N/V constant.



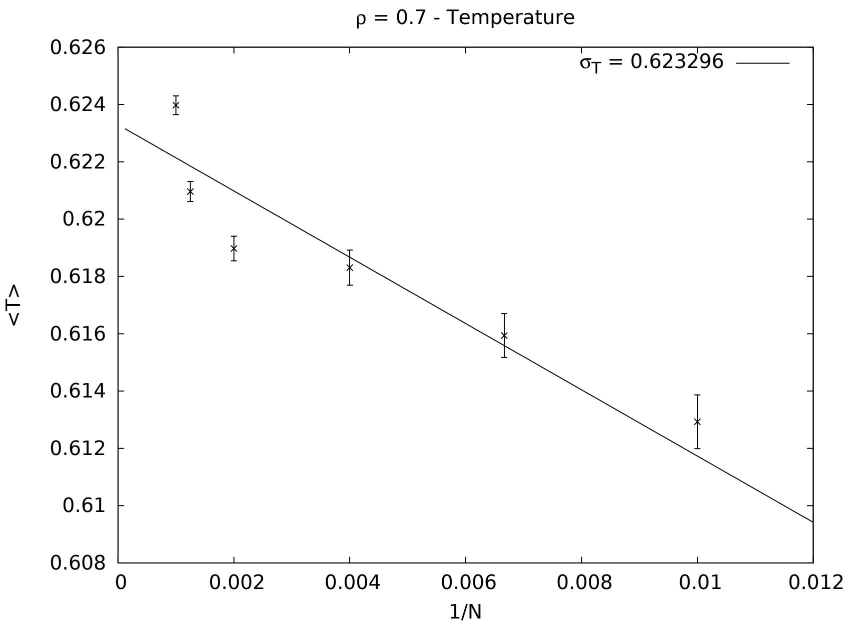


Figure 11. Plot of the potential energy (top) and of the temperature (bottom) as functions of the parameter $1/N$ with $N = 100, 150, 250, 500, 800, 1000$. Each point is obtained as the averege over a simulation run of time $t = 100$ with samples taken once every 100 steps $\Delta t = 0.001$. The errorbars are computed as the standard errors on the mean values. The thermalization time is $t_{\text{therm}} = 10$.

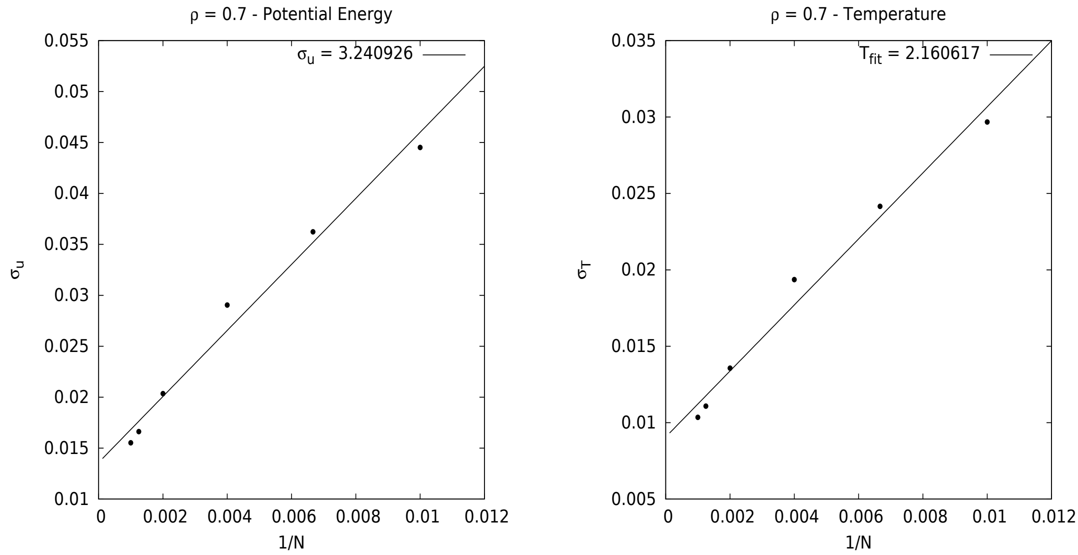


Figure 12. Plot of the standard deviation of the potential energy (left) and of the temperature (right) as funtions of the parameter $1/N$ for $N = 100, 150, 250, 500, 800, 1000$.

The results are:

$$u_{\text{fit}} = -3.9149 \pm 0.0016 \tag{18}$$

$$T_{\text{fit}} = 0.6233 \pm 0.0011 \tag{19}$$

Remark: since the mechanical energy is constant, T and U are related by:

$$\frac{H}{N} = \frac{d}{2} T + u = -2.98 \tag{20}$$

and follows that the fluctuations of the two quantities must cancel out:

$$\Rightarrow \quad \frac{3}{2} \sigma_T = \sigma_u \tag{21}$$

σ_u	3.240926
σ_T	2.160617

$\longrightarrow$ $\frac{\sigma_u}{\sigma_T} = 1.5$