Laboratory of Computational Physics

by Luca Cassia

Dipartimento di Fisica, Università di Milano-Bicocca
I-20126 Milano, Italy

Email: l.cassia@campus.unimib.it

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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:

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

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:

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

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

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

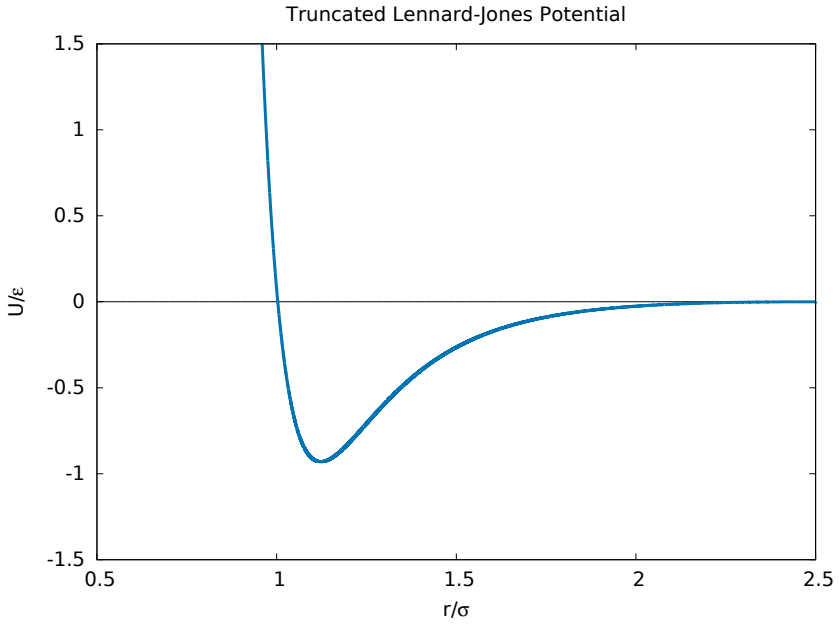

Figure 1. Plot of the truncated L-J potential.

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 $kT = \frac{2}{d}K$ can then be set to a desired value kT' by rescaling the momenta as:

$$p_i \to p_i' = p_i \sqrt{\frac{kT'}{kT}} \tag{7}$$

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.

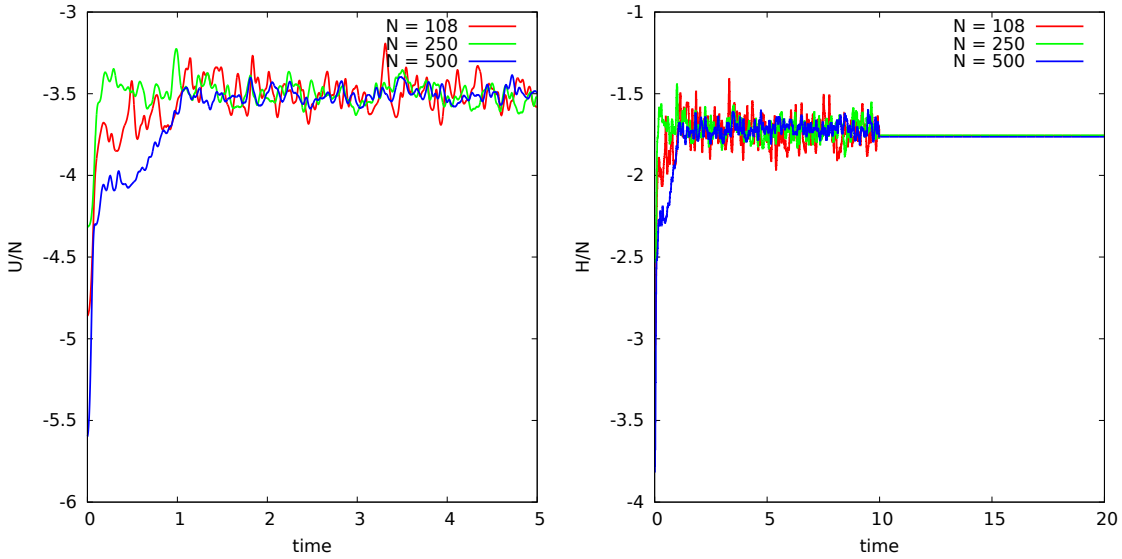

Figure 2. Thermalization of a system of softcore particles at density $\rho = 0.7$, $kT = 1.19$ for $N = 108, 250, 500$. On the left we show the evolution of the density of potential energy U/N in the first 5000 integration steps. On the right is the total energy density H/N, first during the thermalization 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:

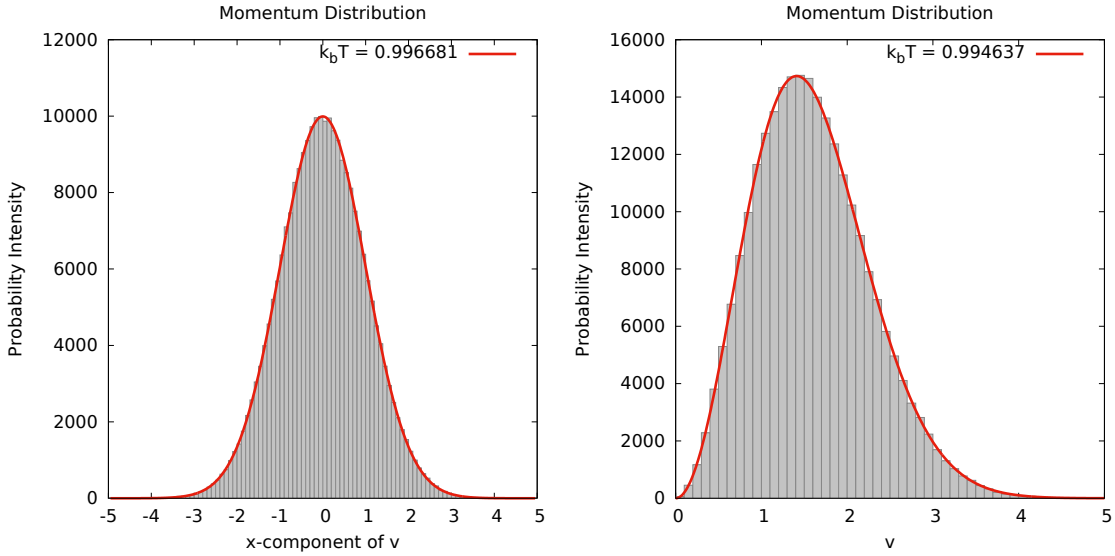

Figure 3. Momentum distributions for a system of $N = 250$ particles at $\rho = 0.5$ and $k_bT = 1.0$. On the left is the v_x distribution and on the right is the distribution of the modulus of the momentum. The measurements were taken every 100 evolution steps for 10^5 steps, each time collecting the momenta of every particle thus giving a total of 250000 samples. The simulation was preceded by a thermalization phase of $t_{\rm therm} = 5000\,\Delta t = 5$. 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 $k\,T = 1.19$.

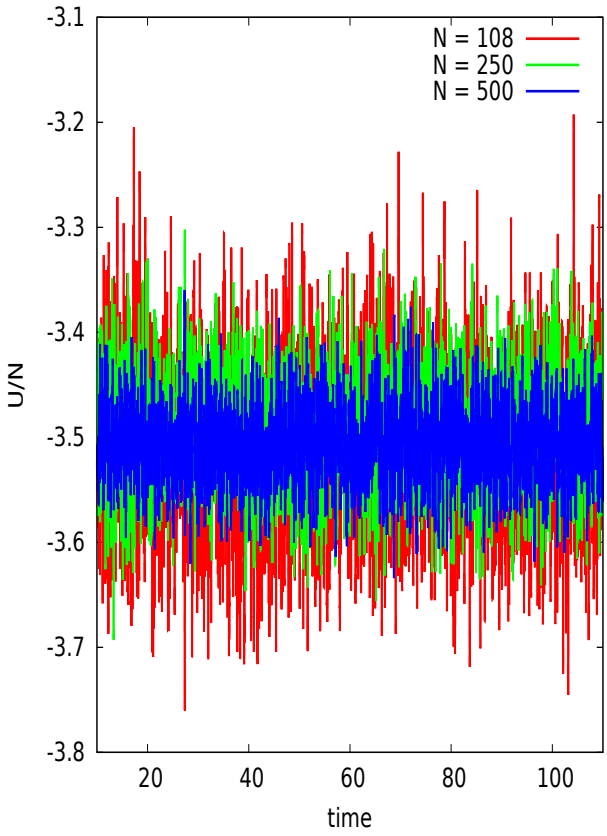

Figure 4. Internal energy density u for $N = 108, 250, 500$ at $\rho = 0.7$ and $kT = 1.19$. Thermalization time $t_{\text{term}} = 10$ and total time of the simulation $t = 100$ ($\Delta t = 0.001$). During the thermalization phase the momenta were rescaled every 10 steps in order to fix the temperature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

1.5 Mean Squared Displacement

1.6 Thermodynamic Limit