Project 3: Molecular dynamics*

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1. Simulating Argon as a Lennard-Jones fluid

1.1. Equations of motion

We consider a system of $N = 864$ particles, enclosed in a cube of side length L, with periodic boundary conditions interacting through a two-body potential of the Lennard-Jones type

$$V(r) = 4\epsilon \left(\frac{\sigma}{r}\right)^6 \left(\left[\frac{\sigma}{r}\right]^6 - 1\right). \tag{1}$$

The total potential energy is thus

$$V(r) = 2\epsilon \sum_{i=1}^{N} \sum_{j \neq i} \left(\frac{\sigma}{r_{ij}}\right)^6 \left(\left[\frac{\sigma}{r_{ij}}\right]^6 - 1\right) \tag{2}$$

the reduction of the factor from 4 to 2 taking into account the double counting in the sums; and the net force on the i-th particle is given by

$$\begin{aligned} \boldsymbol{F}_i(r_{ij}) &= -\frac{\partial V(r)}{\partial \boldsymbol{r}_i} = -\frac{2}{\sigma}\epsilon \sum_{j=1}^{N} \sum_{k \neq j} \left(-12\left[\frac{\sigma}{r_{jk}}\right]^{13} + 6\left[\frac{\sigma}{r_{jk}}\right]^{7}\right) \frac{\partial r_{jk}}{\partial \boldsymbol{r}_i} \\ &= \frac{48\epsilon}{\sigma} \sum_{j \neq i} \frac{\boldsymbol{r}_i - \boldsymbol{r}_j}{\sigma} \left(\left[\frac{\sigma}{r_{ij}}\right]^{14} - 0.5\left[\frac{\sigma}{r_{ij}}\right]^{8}\right) \end{aligned} \tag{3}$$

where

$$\frac{\partial r_{jk}}{\partial \boldsymbol{r}_i} = \frac{\partial}{\partial \boldsymbol{r}_i}\sqrt{(\boldsymbol{r}_j - \boldsymbol{r}_k)^2} = \frac{\boldsymbol{r}_j - \boldsymbol{r}_k}{r_{jk}} \left(\delta_{ij} - \delta_{ik}\right). \tag{4}$$

The equations of motion are then

$$m\frac{\mathrm{d}^2 \boldsymbol{r}_i}{\mathrm{d}t^2} = \sum_{j \neq i} \boldsymbol{F}_i(r_{ij}) \tag{5}$$

*Code for the following tasks can be found at the repository: `https://github.com/VictorG20/comphysics.git`

1.2. Dimensionless units and discretization method

If we define the dimensionless variables

$$\boldsymbol{r}^* = \frac{\boldsymbol{r}}{\sigma}, \qquad t^* = \frac{t}{\tau} \tag{6}$$

our equations of motion in terms of them read

$$\frac{\mathrm{d}^2\boldsymbol{r}^*}{\mathrm{d}t^{*2}} = \tau^2 \frac{48\epsilon\sigma^{-2}}{m} \sum_{j\neq i} (\boldsymbol{r}_i^* - \boldsymbol{r}_j^*) \left({r_{ij}^*}^{-14} - 0.5 {r_{ij}^*}^{-8} \right). \tag{7}$$

Finally, using the mass of the argon $m = 6.6335209 \times 10^{-26}$kg, we take time in units of τ as

$$\tau = \sqrt{\frac{m}{48\epsilon\sigma^{-2}}} = 3.11203 \times 10^{-13}\text{sec.} \tag{8}$$

and we get the equation of motion in dimensionless variables as

$$\frac{\mathrm{d}^2\boldsymbol{r}_i^*}{\mathrm{d}t^{*2}} = \boldsymbol{f}_i(r_{ij}) = \sum_{j\neq i} (\boldsymbol{r}_i^* - \boldsymbol{r}_j^*) \left({r_{ij}^*}^{-14} - 0.5 {r_{ij}^*}^{-8} \right). \tag{9}$$

Density and unit cell characteristics: The dimensionless density is given by

$$\rho = \frac{N \cdot m}{L^3}, \qquad L^* = \frac{L}{\sigma} \implies \rho^* = \frac{\rho\sigma^3}{m} = \frac{N}{L^{*3}}. \tag{10}$$

Therefore, if the number of particles is set, the length of the box in units of σ is

$$L^* = \left(\frac{N}{\rho^*} \right)^{1/3}. \tag{11}$$

Since we are going to set the particles at the nodes of a face-centered cubic lattice configuration with boundary conditions, the number of unit cells, n, required to place them is

$$N = 4n^3. \tag{12}$$

Hence, given that the length of the box must equal na,

$$L^* = na = (N/4)^{1/3} a \implies a = (4/N)^{1/3} L^* = (4/\rho)^{1/3}. \tag{13}$$

Velocity distribution: In order to generate the initial velocities through a Gaussian distribution we use

$$p(\mathbf{v}) \sim \exp\left(-\frac{m\mathbf{v}^2}{2k_B T} \right) = \exp\left(-\frac{\mathbf{v}^{*2}}{2T^*} \frac{m\sigma^2}{\epsilon\tau^2} \right) = \exp\left(-\frac{1}{2} \frac{\mathbf{v}^{*2}}{T^*/48} \right) \implies \begin{cases} \mu = 0, \\ \sigma_v = \sqrt{T^*/48} \end{cases} \tag{14}$$

Temperature: The temperature is, at time t, given by the equipartition theorem (in dimensional variables) as

$$\frac{3}{2} N k_B T = \frac{1}{2} \sum_{i=1}^{N} m\mathbf{v}_i^2 \implies T = \frac{1}{3Nk_B} \sum_{i=1}^{N} m\mathbf{v}_i^2 \tag{15}$$

or, in dimensionless variables

$$T^* = \frac{k_B T}{\epsilon} = \frac{1}{3N} \sum_i \frac{m}{\epsilon} \frac{\sigma^2}{\tau^2} \mathbf{v}_i^{*2} = \frac{16}{N} \sum_{i=1}^{N} \mathbf{v}_i^{*2}. \tag{16}$$

Discretization method: Instead of the algorithm present in the paper, to integrate the equations of motion we use the Velocity Verlet algorithm in the following form

$$\tilde{\mathbf{v}}(t) = \mathbf{v}(t) + \frac{h}{2}\mathbf{f}(t) \quad \Rightarrow \quad \mathbf{r}(t+h) = \mathbf{r}(t) + h\tilde{\mathbf{v}}(t) \quad \Rightarrow \quad \mathbf{f}(t+h) = \mathbf{f}[\mathbf{r}(t+h)] \tag{17}$$

$$\Rightarrow \quad \mathbf{v}(t+h) = \tilde{\mathbf{v}}(t) + \frac{h}{2}\mathbf{f}(t+h) \tag{18}$$

where h is the time increment which we take equal to 0.032.
Bookkeeping device: Every nth step, compute all the $\frac{1}{2}N(N-1)$ distances, and, given a particle i, we make a table of all the particle which are within a distance r_M of that particle. Then, for the next $n-1$ steps in time, take into account only the particles in the tables.

a) Run a simulation with $T_0^* = 1.38$ and $\rho^* = 0.55$ for a total time of $t^* = 1$, and plot the melting factor ρ_k against time. For the initial fcc lattice configuration, you should get $\rho_k = 3N$. Furthermore, plot the distribution of each velocity component at the end of the simulation and discuss your result. (6 points)

The melting factor ρ_k against time is shown in Fig.1. From it we can see that it is indeed decreasing in time, corresponding to the system being driven away from a solid-like state configuration (the initial fcc configuration) to a fluid-like one.

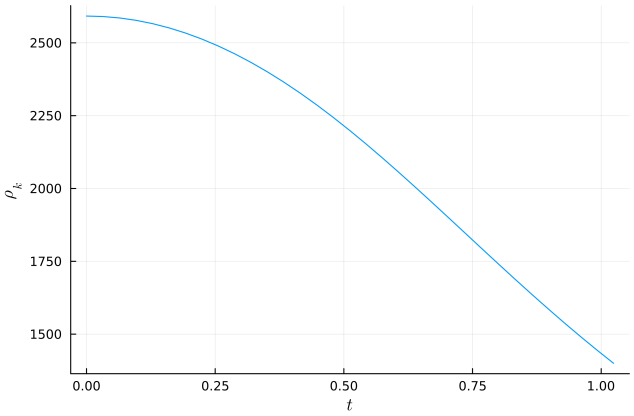

Figure 1: Melting factor versus time.

For the final velocity components, we have their normed histograms, as well as the fitting Gaussian curves, in Fig.2. From the distributions and the given values for the means and standard deviations we see that the velocity is still isotropic and that the (dimensionless) temperature is $T^* \approx 48 * (0.158)^2 = 1.1982$, indicating that the temperature has decreased from the given initial one.

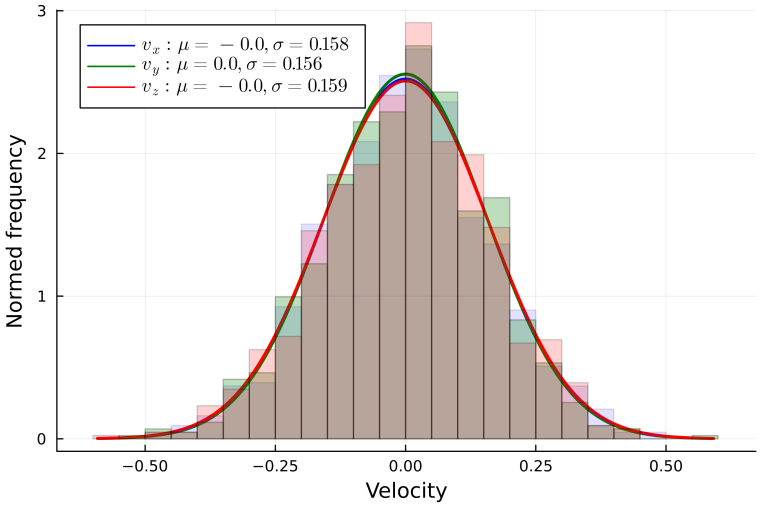

Figure 2: Distribution of the components of the velocity and the fitting Gaussian distributions.

b) Implement the neighborhood tables as suggested by Verlet and report the speed-up you can achieve. Use the suggested parameters, i.e. $r_M^* = 3.3$ and $n = 16$. (4 points)

The difference in running time between using the book-keeping algorithm is shown in Fig.3. It represents an improvement of 84% over the time when computing all forces or, in other words, a cut of the computing time by a factor of the order of 10.

Running benchmarks with and without book-keeping

```
T = 1.38
ρ = 0.55
t_final = 48.
book_keeping = false

@benchmark simulation(T, ρ, t_final, book_keeping)
```

```
BenchmarkTools.Trial: 1 sample with 1 evaluation.
 Single result which took 156.055 s (13.81% GC) to evaluate,
 with a memory estimate of 461.22 GiB, over 6189069865 allocations.
```

```
T = 1.38
ρ = 0.55
t_final = 48.
book_keeping = true

@benchmark simulation(T, ρ, t_final, book_keeping)
```

```
BenchmarkTools.Trial: 1 sample with 1 evaluation.
 Single result which took 25.462 s (14.60% GC) to evaluate,
 with a memory estimate of 75.10 GiB, over 1005697989 allocations.
```

Figure 3: Differences in time when running the algorithm with and without book-keeping.

c) Run a simulation with $T_0^* = 1.38$ and $\rho^* = 0.55$ for a total time of $t^* = 48$, and plot the temperature T^* against time. When is the system equilibrated? Calculate the time average $\langle T^* \rangle$, ignoring measurements before equilibration. Discuss your results, in particular comparing $\langle T^* \rangle$ to T_0^*. (6 points)

The evolution of the temperature in time is given in Fig.4. Equilibrium can be seen to be reached after the first 5 units of time t^*. Such value is roughly after the first 55 time steps. The reason to declare equilibrium after this point (or for values close to it), is due to the oscillatory behaviour that is shown after. The average temperature in equilibrium is found to be $\langle T^* \rangle \approx 1.32$, which is below the initial temperature considered for the distribution of the velocities. This represents partly what has been discussed in part a), namely that the melting factor decreasing has led to a sharper distribution of the velocities, thereby decreasing the possibilities for them to obtain values as high as the original ones. This also represents that the average of the kinetic energy has come closer to its value given by the virial theorem.

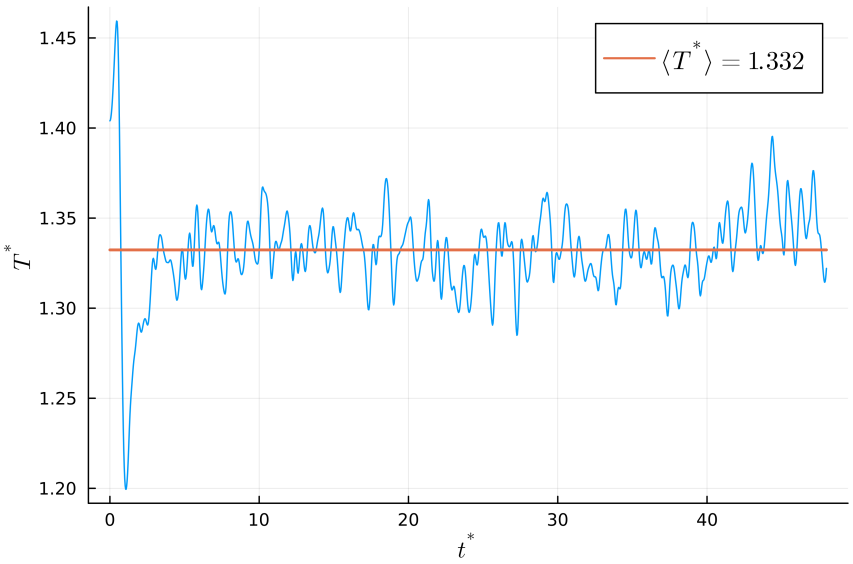

Figure 4: Evolution of the temperature in time and its average during equilibrium.

d) Implement a momentum re-scaling, which kicks in occasionally during the equilibration (e.g. every 20 steps) to drive the temperature towards T_0^*. Then repeat the simulation and analysis made in part c), again comparing $\langle T^* \rangle$ with T_0^*. (6 points)

Having implemented the re-scaling of the velocities every $n = 20$ steps we obtain the evolution in Fig.5. From this we see that now we do obtain the desired temperature, $T_* = 1.38$, as the average temperature once equilibrium has been reached.

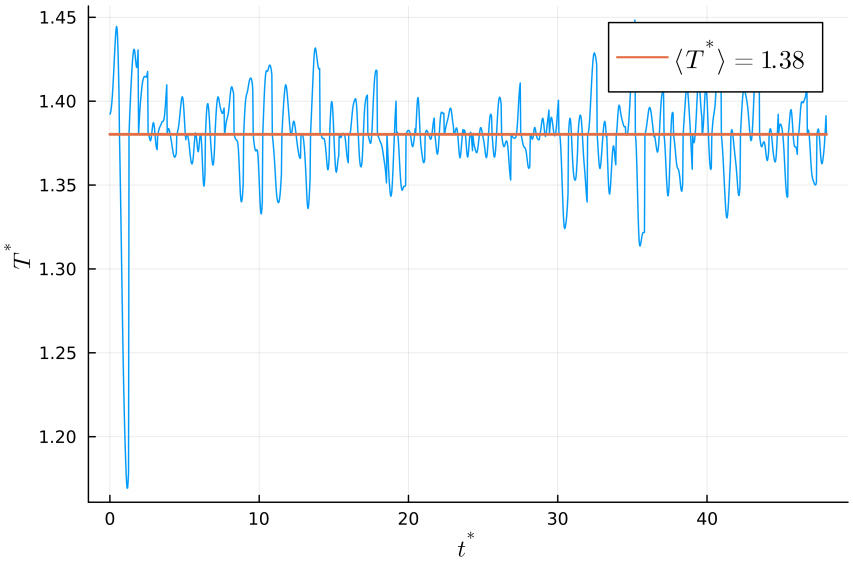

Figure 5: Evolution of the temperature in time and its average during equilibrium.