

Molecular dynamics of a classical fluid: Part 2

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We continue with a system of N classical particles with mass m interacting via the 6-12 Lennard-Jones pair potential:

$$u_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] . \quad (1)$$

which we have appropriately shifted to make it short range. You have expressed the problem in reduced units so that the basic units of length, energy, and mass are σ , ϵ , and m , respectively. Using reduced units simplifies the problem but also allows one to use the same simulation to study different systems: For instance, the same simulation at $T = 0.5$ and $\rho = 0.5$ can be used to study Ar at 60 K and a density of 849 kg/m³, and Xe at 112 K and a density of 1617 kg/m³.

If you have completed Part 1, you should have a molecular dynamics (MD) working code for a Lennard-Jones model, which can compute the instantaneous potential, kinetic, total energy, and temperature of the system as well as their time averages (after discarding an appropriate equilibration time). Following the equipartition theorem, we defined an instantaneous temperature in terms of the instantaneous kinetic energy as

$$T(t) = \frac{2}{3N} K(t) \quad \text{and} \quad T = \langle T \rangle = \frac{2}{3N} \langle K(t) \rangle . \quad (2)$$

We will further modify the code and move in the phase diagram of a Lennard-Jones liquid, which is shown for the gas-liquid transition in Figure 1.

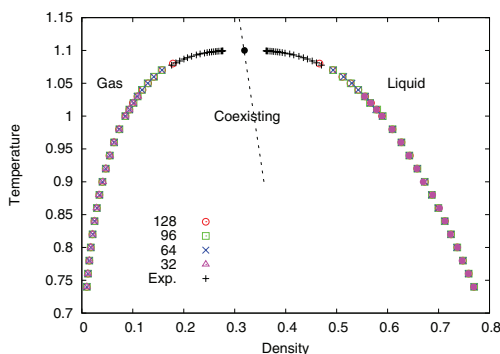


Figure 1: MD simulations of the gas-liquid phase boundaries with different values of L_x in a system with $N = L_x \times L_x \times 2L_x$ particles. From H. Watanabe *et al.*, “Phase diagram and universality of the Lennard-Jones gas-liquid system, J. Chem. Phys. **136**, 204102 (2012).

1. In Part 1, you assigned a given temperature T_0 at $t = 0$ by rescaling the initial velocities so that $T(t = 0) = T_0$.

Use $N = 125$, $\rho = 0.7$, and $T_0 = 2$. Choose an appropriate time step¹. Repeat the run a few times and establish the typical deviation from the initial target temperature T_0 . Discard an appropriate N_e steps before computing the averages.

2. We now want to set up the simulation so that the resulting average temperature is reasonably close to the chosen T_0 . Let us do so by splitting the run in three parts:

- N_T steps of preparation, where we thermalize the system at a temperature T .
- N_e steps of equilibration in NVE.
- N_{go} steps of production run in NVE, where you compute the averages.

In the first N_T steps of preparation, rescale the velocities at every step after having moved coordinates and velocities with the velocity-Verlet algorithm. After N_T steps, switch to the microcanonical ensemble.

- a) Do you have conservation of energy during the first N_T steps? Explain your answer.
- b) Use $N = 125$, $\rho = 0.7$, and $T_0 = 2$. Is your estimate of the average temperature closer to T_0 than in the run of Point 1? For which value of N_T do you obtain an average temperature reasonably close to T_0 ?
- c) Use $N = 125$ and $\rho = 0.5$. Consider $T_0 = 2$ and $T_0 = 0.9$. The first temperature is above and the second below the critical point. Check your choice of N_T in the two cases and the obtained average temperature (in comparison with the chosen T_0).

Note: One should not rescale the temperature over the whole run since this would not allow fluctuations in the kinetic energy, which are instead present in the canonical ensemble. There are ways to simulate a system in the canonical ensemble by coupling the particles to a more sophisticated thermostat but this is somewhat difficult and beyond this course.

3. You will now compute the pressure according to the virial formula of which you find the derivation in the “Molecular dynamics primer” notes on blackboard (Page 28).

- i) The virial formula tells you that

$$P = \rho k_B T + \frac{1}{3V} \left\langle \sum_{i=1}^N \mathbf{F}_i \cdot \mathbf{r}_i \right\rangle. \quad (3)$$

Show that, for pairwise interactions, this formula can be rewritten as

$$P = \rho k_B T + \frac{1}{3V} \left\langle \sum_{i=1}^N \sum_{j>i} \mathbf{f}_{ij} \cdot \mathbf{r}_{ij} \right\rangle. \quad (4)$$

Use this last expression to compute the pressure in your code.

¹A good criterion is to choose the time step so that the variation in the energy are smaller (at least two order of magnitude) than the fluctuations of the potential (or kinetic) energy. You can somewhat loosen this requirement but always keep an eye on conservation of energy in your run.

Hint: Compute the pressure inside the function where you evaluate the force as you will be using the same quantities.

- a) Use $N = 125$, $\rho = 0.8$, and $T_0 = 2$. Compute the average pressure (always check that you have discarded a sufficient number N_e of steps). How large is the deviation of P from the value computed from the ideal gas law, $P = \rho k_B T$?
- b) Use $N = 125$ and $T_0 = 2$. Vary ρ up to a value of 0.8. Plot the pressure P as a function of ρ . You have computed the isotherm at $T_0 = 2$. Up to what density is the ideal gas law a good approximation?
- c) Use $N = 125$ and $T_0 = 0.8$. Vary $\rho \in [0.4, 0.8]$. Plot the pressure P as a function of ρ . You are now below the critical temperature and you should observe gas-liquid coexistence (see Figure 1). Therefore, the pressure should be constant for densities inside the coexistence region. What do you observe?

Note: For a finite number of particles, a relatively important free-energy cost is associated with the creation of an interface between the liquid and the gas. For sufficiently small systems, it can be favorable for the system not to phase separate at all.

4. You will now compute the radial distribution function, $g(r)$, which characterizes the local structure of a fluid and can be accessed experimentally for simple liquids via neutron or X-ray scattering.

If one particle is taken to be at the origin, $g(r)$ is the density of particles located at a distance r from the origin, normalized by the average density $\rho = N/V$.

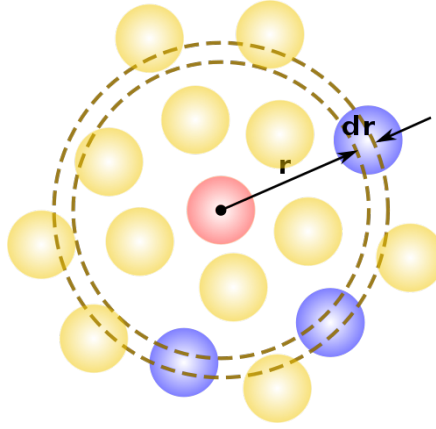


Figure 2: Computation of $g(r)$.

- a) To compute $g(r)$, choose an atom in the system, compute the distance from the other particles, and accumulate them in an histogram vector, where the end indices correspond to $r = 0$ and $r = L/2$ (due to periodic boundary conditions) and the bin size is dr (see Figure 2). Repeat the process for all other atoms. At the end of the run, normalize the histogram at r by the volume of the shell at r .

Use $N = 125$, $\rho = 0.8$, and $T_0 = 2$. Compute and plot $g(r)$.

- b) Compute the average interaction energy of one particle with the other particles as

$$\int u(r) \rho g(r) dr. \quad (5)$$

- c) Explain why the average potential is given by

$$\langle V \rangle = \frac{N}{2} \int u(r) \rho g(r) \, d\mathbf{r} . \quad (6)$$

- d) In the same run, compute the average potential using $g(r)$ and compare it with the average potential you obtain with a direct calculation as you had before.
- e) Using the same reasoning as for the potential energy, express the pressure (Eq. 4) in terms of $g(r)$ and $\frac{du}{dr}$. Explain how you obtain your expression. Compute the pressure using $g(r)$ and compare it with the value you obtain in the same run using a direct calculation as you have done before.
- f) Set $N = 125$ and $T_0 = 2$. Compare the $g(r)$ you obtain with $\rho = 0.1$ and $\rho = 0.8$. Plot your results and discuss the differences.