

Molecular dynamics simulation of the Lennard-Jones fluid

In class we discussed many practical aspects of molecular dynamics simulations in the context of a model fluid, defined by the Lennard-Jones pair interaction potential:

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

Here you will put those considerations to work, developing your own molecular dynamics code and using it to explore the statistics of molecular motions.

(i) Write a program that advances the positions and momenta of $N \geq 200$ particles in a cubic box of side length L . You should be able to reuse a significant amount of code from previous assignments, for example in implementing periodic boundary conditions.

Since the Lennard-Jones potential does not have a finite range, it must be truncated at some distance r^* . We therefore consider a modified potential

$$u(r) = \begin{cases} u_{\text{LJ}}(r) - u_{\text{LJ}}(r^*), & r < r^* \\ 0, & r > r^* \end{cases}$$

that limits the number of pair interactions. For this assignment, use $r^* = 2.5\sigma$. Because this cutoff distance is smaller than any value of $L/2$ you will consider, the complete set of interactions involves only the closest periodic images of each pair of particles.

Use the Verlet algorithm to propagate dynamics with a dimensionless time step $\Delta t^* = \Delta t/\tau = 0.001$, where $\tau = \sqrt{m\sigma^2/\epsilon}$ is the unit of time. As units of length and energy, use σ and ϵ , respectively. You should find that these choices render the Verlet equations very clean.

Assign and adjust velocities so that the system eventually reaches thermal equilibrium at a reduced temperature $T^* = k_{\text{B}}T/\epsilon = 1.5$. As discussed in class, the simplest scheme for doing so is to periodically rescale velocities until the kinetic energy no longer drifts but instead fluctuates about a stable value consistent with the target temperature.

Once you are convinced that your system has reached thermal equilibrium, perform the Verlet integration without velocity rescaling. To provide evidence that your simulation is working properly, make a plot of the kinetic, potential, and total energies as a function of time along a trajectory of length $t = 5\tau$ at density $\rho\sigma^3 = 0.8$. You should find that energy is well conserved on the scale of natural variations in the potential and kinetic energies.

(ii) For a chaotic system, integrating Newton's equations of motions is tantamount to sampling the micro-canonical ensemble. In the limit $N \rightarrow \infty$ statistics in this ensemble are for the most part indistinguishable from those of the more mathematically convenient canonical ensemble, in which energy can be exchanged with a heat bath at temperature T .

Test this equivalence by calculating a distribution of particle velocities from your molecular dynamics simulations. Specifically, compute a normalized histogram $P_{\text{MD}}(v_x)$ of the x -component of a particle's velocity at a temperature $T^* = k_{\text{B}}T/\epsilon = 1.5$ and density $\rho\sigma^3 = 0.8$. Plot your result. (Be sure to exploit pertinent symmetries.)

Compare your estimate of $P_{\text{MD}}(v_x)$ with that expected from fluctuations in a canonical ensemble. Repeat the calculation for $T^* = 1.5$ and $\rho\sigma^3 = 0.3$.

(iii) In a previous assignment you computed the radial distribution function $g(r)$ for the hard sphere fluid at several densities, using statistics collected from Monte Carlo sampling. With the sampling provided by your molecular dynamics simulations, calculate $g(r)$ in the same manner for the Lennard-Jones fluid at densities $\rho\sigma^3 = 0.3, 0.6$, and 0.8 and temperature $T^* = 1.5$. Plot your results, and describe qualitative similarities with and differences from the case of hard spheres. How would you expect $g(r)$ to change at higher temperatures? (Feel free to try it out!) Explain your reasoning for both the hard sphere and Lennard-Jones systems.

(iv) For the same thermodynamic states considered in part (iii), calculate the mean squared displacement $\langle \Delta r^2(t) \rangle \equiv \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle$ of a tagged particle i as a function of time. Plot your results over a range of time in which your results are statistically robust (i.e., you obtain similar results from different runs). Make sure this range extends to sufficiently long times that diffusive behavior is evident. Include error bars on the plot to illustrate that your results are statistically trustworthy. A simple estimate of sampling error (e.g., the standard deviation from several independent trials) is sufficient.

(v) For the same thermodynamic states considered in part (iii), calculate the velocity correlation function $C_{vv}(t) \equiv \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle$ of a tagged particle i as a function of time. Make plots spanning the same time range as in part (iv). Again include error bars.

(vi) In class we showed that the diffusion coefficient D can be obtained either from the long-time behavior of $\langle \Delta r^2(t) \rangle$, or alternatively from the integrated time dependence of $C_{vv}(t)$. Perform both of these calculations, for each of the thermodynamic states you have considered. Present your results in a table, and provide estimates of random error in the values of D you have determined.