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Computational Molecular Physics **Winter 2017/18**

Problem set 1 **2 November 2017**

Problem 1.1 *Thermodynamics*

Simulation data for a simple fluid are provided in the file `lj.h5`. The N particles have mass m and interact via the truncated and shifted Lennard-Jones pair potential

$$V(r) = [u_{\mathrm{LJ}}(r) - u_{\mathrm{LJ}}(r_c)]\theta(r_c - r)\,, \qquad u_{\mathrm{LJ}}(r) = 4\varepsilon\Big[(r/\sigma)^{-12} - (r/\sigma)^{-6}\Big]\,,$$

with $r_c = 2.5\sigma$. The units of length, time, and energy are σ, $\sqrt{m\sigma^2/\varepsilon}$, and ε, respectively.
Note: The data are stored in the H5MD format, which is described at `https://nongnu.org/h5md` and can be accessed with any API for HDF5 files, e.g., `h5py` in Python.

a) Use the data in `particles/` to calculate the following thermodynamic quantities: mass density ϱ, temperature T, pressure P, internal energy per particle U/N (or total energy).

b) Calculate and plot the pair correlation function $g(r)$ of the fluid and indicate the effective particle diameter. Repeat your calculation with only 1/10 of the available particles and estimate the statistical uncertainty.

c*) The file contains also time series' of the potential and kinetic energies per particle obtained from a canonical (NVT) simulation. Find the isochoric specific heat $c_V = N^{-1}(\partial U/\partial T)_V$ from the relation $(\Delta E)^2 = Nk_BT^2c_V$, where $(\Delta E)^2$ denotes the variance of the total energy. Map your results to methane using $\sigma = 3.73\,\text{Å}$, $m = 16\,\mathrm{g/mol}$, and $\varepsilon/k_B = 148\,\mathrm{K}$.

Problem 1.2 *Hamiltonian dynamics*

The motion of a mass $m = 1\,\mathrm{g}$ connected to a harmonic spring with spring constant $k = 0.1\,\mathrm{N/m}$ is governed by the canonical equations

$$\dot{x}(t) = p(t)/m\,, \qquad\qquad \dot{p}(t) = -kx(t)\,,$$

where $x(t)$ denotes the displacement from the equilibrium position at time t and $p(t)$ the momentum. Solve this set of linear differential equations numerically using *(i)* Euler's algorithm, and *(ii)* the velocity-Verlet algorithm.

a) Consider time from $t = 0$ to 10 seconds and timesteps $\Delta t = 10^{-3}\,\mathrm{s}$ with the initial conditions $x(0) = 0$ and $p(0) = 10^{-3}\,\mathrm{kg\cdot m/s}$. Plot your numerical solutions as a function of time and compare with the analytical result. Plot the trajectories in phase space, i.e., momentum $p(t)$ vs. displacement $x(t)$. Discuss your results.

b) Compute solutions for different timesteps (e.g., $\Delta t = 10^{-k/3}\,\mathrm{s}$ for $k = 6, 7, 8, \dots$) using both algorithms. Compare the results, which timestep do you find satisfactory? How does your choice relate to the eigenfrequency of the oscillator, $\omega_0 = \sqrt{k/m}$?

c) Calculate the numerically obtained total energy $E(t)$ and plot the deviation $\Delta E(t) := E(t) - E(0)$ for the previous results. Also plot $\Delta E(t)/\Delta t$ and $\Delta E(t)/(\Delta t)^2$ for the different timesteps. Which algorithm would you suggest for molecular dynamics simulations?

d*) Determine the corresponding Liouville operator. Express both integration algorithms by splitting formulas and argue that the Euler algorithm is not invariant under time reversal ($t \mapsto -t$, $v \mapsto -v$). Test this numerically by reverting the integration.

Due date: ***9 November, 12 p.m.***