Chapter 4

List of exercises

1 Sampling

1.1 Exercise: Sampling random points within D- dimensional domains by hit and miss

Rectangle Generate random points uniformly distributed within a rectangle $[a, b] \times [c, d]$ and compare the analytic value of the area $A = L_{ab} L_{cd}$ with the Monte Carlo estimate based on the hit-miss method as a function of the number of "throws".

Disk Do the same for a unit radius disk.

Sampling random numbers from a given distribution

1.2 Exercise: Inversion method

Use the inversion method to design an algorithm that samples random numbers according to the power law probability distribution

$$\rho(x) = c\, x^n, \quad \text{with } x \in [0, 1] \tag{4.1}$$

for some constant c that normalise $\rho(x)$. Simulate the cases $n = 3, 4$ and compare the histograms with the analytical expressions.

1.3 Exercise: Inversion method II

Use the inversion method to sample random numbers according to the probability distribution $\rho(x) = cx^2$ with $x \in [0, 2]$

1.4 Additional exercises

Use the inversion method to generate random numbers with the following PDF

1. $\rho(x) = \mu\, e^{-\mu\, x}$, for $x \geq 0$;
2. $\rho(x) = 2x\, e^{-x^2}$, for $x \geq 0$.
3. $\rho(x) = \frac{1}{(a+bx)^n}$ for $x \geq 0$ and $n > 1$

Note. *For all the exercises proposed above first compute the F, F^{-1} and the map $x_i = f(\xi_i)$ and then implement and run the corresponding algorithm. Compute the histogram of the sampled points and compare it with the expected PDF.*

2 Sampling via transformation of coordinates

2.1 Exercise: Sampling uniformly points within a unit radius disk

The obvious approach to sample points within the unit disk corresponds to considering $r = \xi_1$ and $\theta = 2\pi\xi_2$ with ξ_1, ξ_2 uniformly distributed in $[0, 1]$.

- Show by simulation that this algorithm does not sample points uniformly within the disk. Explain which is the conceptual mistake of this algorithm.
- Design an algorithm that does it correctly. (**Hint:** One way is to first perform the transformation into polar coordinates and then use the marginal $p(r)$ and the conditional $p(\theta|r)$ PDFs to do the sampling by applying in turn the 1D inversion method.)

2.2 Exercise: Box-Muller transformation

A way to generate numbers from a 2D (normalised) 2D Gaussian PDF, $\mathcal{N}(0, 1)$ is the so-called Box-Muller transformation. This is based on the idea presented during the lecture in which one first makes a coordinate transformation to factorize the 2-point PDF

$$\rho(x, y) = \frac{1}{2\pi} e^{-(x^2+y^2)/2} \tag{4.2}$$

into a product of two one-point PDFs and then performs two separate samplings, one for each PDF.

- Write an algorithm that does this sampling by first performing the analytical calculations necessary to find the correct transformation;
- How one can extend the algorithm to sample from $\mathcal{N}(\mu, \sigma^2)$?

2.3 Exercise: Rejection method

Use the rejection method to generate random numbers that are distributed according to the pdf

$$f(x) = \sqrt{2/\pi}\, e^{-x^2}. \tag{4.3}$$

Hint: One may use a function $g(x) = A$ for $0 \leq x \leq p$ and $g(x) = (A/p)\, x\, \exp\left(p^2 - x^2\right)$ for $x > p$. See how good the performance is for a few values of p (use a reasonable value N of "darts".

3 Importance sampling

3.1 Exercise

Let us consider the following function $f(x) = e^{-x^2} g(x)$ in $[0, \infty]$ where $g(x)$ is a slowly varying function. Compute the integral both with the crude method and by using the importance sampling technique. Hint: For the importance sampling method use a Gaussian random number generator with density $W(x) = \sqrt{2/\pi} e^{-x^2}$ With this choice one has

$$I = \int_0^\infty f(x)\, dx \sim \frac{1}{N} \sum_{i=1}^{N} \frac{f(x_i)}{W(x_i)} = \frac{1}{N} \sqrt{\pi/2} \sum_{i=1}^{N} g(x_i). \tag{4.4}$$

3.2 Exercise

Estimate the integral

$$\int_0^{\pi/2} \cos\, x\, dx \tag{4.5}$$

using the importance sampling technique with $g(x)$ proportional to $a + bx^2$. Determine the optimal values of the parameters a and b to generate samples according to $g(x)$ and establish the number of iterations needed to get an accuracy of $\%1$.

3.3 Exercise

Let us consider the function $f(x)$ defined as

$$f(x) = \begin{cases} 0 & \text{for} \quad x < T \\ 1 & \text{for} \quad x \geq T \end{cases} \tag{4.6}$$

and compute the average

$$\langle f \rangle_\rho = \int_{\mathbb{R}} f(x)\, \rho(x)\, dx \tag{4.7}$$

with respect to the PDF $\rho(x) = e^{-x}$ defined for $x \geq 0$. Notice that while the function $f(x)$ is zero for $x < T(= 5)$ the PDF $\rho(x)$ is very high in that region. This means that most values x sampled according to $\rho(x)$ will be zero. On the other hand $f(x) = 1$ for $x > T(= 5)$ where the $\rho(x)$ is very small. We can try to get an estimate of $\langle f \rangle_\rho$ via importance sampling. Consider the function $g(a, x) = a \exp(-ax)$ defined for $x \geq 0$ and for $0 < a \leq 1$ where a is the parameter to optimise according to a minimum variance principle.

- Show analytically that

$$\begin{aligned} \langle f \rangle &= e^{-T} \\ \sigma^2(f) &= \langle f \rangle (1 - \langle f \rangle) \\ \sigma^2\left(a, f(x)\rho(x)/g(a,x)\right) &= \frac{e^{-T(2-a)}}{a(2-a)} - e^{-2T} \end{aligned} \tag{4.8}$$

- Find the value of a, a^* such that the variance $\sigma^2\left(a, f(x)\rho(x)/g(a,x)\right)$ is minimum.

- Discuss the improvement one can get in the statistical errors in the cases $T = 3, 5, 10$ and 20. This can be done by comparing the values $\sigma(f)/\langle f \rangle$, $\sigma\left(f(x)\rho(x)/g(a^*, x)\right)$, and $\sigma(f)/\sigma\left(f(x)\rho(x)/g(a^*, x)\right)$ for $T = 3, 5, 10$ and 20.

4 Markov chains

4.1 Exercise

We have seen that the state probability vector of a Markov chain μ_n satisfies the recurrence relation

$$\mu_n = \mu_{n-1}\,\mathcal{P} \tag{4.9}$$

Show that this equation is equivalent to write

$$\mu_n(i) = \left(1 - \sum_{j\in S\, j\neq i} p_{j,i}\right)\mu_{n-1}(i) + \sum_{j\in S\, j\neq i} p_{i,j}\mu_{n-1}(j). \tag{4.10}$$

What does it say this equation?

4.2 Exercise: digraph

Draw the digraphs and classify the states of the Markov chains defined by the following transition matrices:

(A)

$$\mathcal{P} = \begin{pmatrix} 0 & 0.5 & 0.5 \\ 0.5 & 0 & 0.5 \\ 0.5 & 0.5 & 0 \end{pmatrix} \tag{4.11}$$

(B)

$$\mathcal{P} = \begin{pmatrix} 0 & 0 & 0.5 & 0.5 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \tag{4.12}$$

(C)

$$\mathcal{P} = \begin{pmatrix} 0.3 & 0.4 & 0 & 0 & 0.3 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0.6 & 0.4 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 \end{pmatrix} \tag{4.13}$$

4.3 Exercise: irreducible

Given the two Markov chains defined by the following transition matrices

$$\begin{aligned} \mathcal{P}_1 &= \begin{pmatrix} 1/2 & 1/2 \\ 1 & 0 \end{pmatrix} \\ \mathcal{P}_2 &= \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1/4 & 0 & 3/4 \end{pmatrix} \end{aligned} \tag{4.14}$$

verify whether they are irreducible and in case compute their period. Moreover,for both of them compute $(\mathcal{P})^n$ and the limit $\lim_{n\to\infty}$ (or the limit of its average).

4.4 Exercise: regularity

- Given the Markov chain defined by

$$\mathcal{P} = \begin{pmatrix} 1/2 & 1/4 & 1/4 \\ 1/2 & 0 & 1/2 \\ 1/4 & 1/4 & 1/2 \end{pmatrix} \tag{4.15}$$

  show that is regular.

- Is the Markov chain defined by

$$\mathcal{P} = \begin{pmatrix} 1 & 0 \\ 1/2 & 1/2 \end{pmatrix} \tag{4.16}$$

  regular?

4.5 Exercise: Stationarity

A

Let $0 < p < 1$ and let us consider a Markov chain defined on the finite space $S = \{1, 2, 3, 4\}$ by the transition matrix

$$\mathcal{P} = \begin{pmatrix} p & 1-p & 0 & 0 \\ 0 & 0 & p & 1-p \\ p & 1-p & 0 & 0 \\ 0 & 0 & p & 1-p \end{pmatrix} \tag{4.17}$$

- Show that the Markov chain is recurrent irreducible
- Show that the Markov chain is aperiodic (consider for instance the term p_{11}
- Compute the fixed point π that, given the first two points, is the invariant unique distribution of the Markov chain.

B

Find the stationary distribution π of the Markov chain with transition matrix

$$\mathcal{P} = \begin{pmatrix} 1/2 & 1/2 & 0 \\ 1/4 & 1/2 & 1/4 \\ 0 & 1/2 & 1/2 \end{pmatrix} \tag{4.18}$$

5 Simulation of a 2D Ising model by the Metropolis algorithm

5.1 Exercise

Program Write a program that simulates a 2D Ising model with periodic boundary conditions by using the Metropolis acceptance matric a_{ij} and the matrix Γ_{ij} based on the local spin-flip (Glauber) proposed move.

Simulation By assuming $k_B = 1$ and $J = 1$ simulate the 2D Ising model for different values of temperatures (at least 3, one below, one above, and one close to the critical temperature $T_c = \frac{2}{\ln\left(1+\sqrt{2}\right)}$ and 3 different values of L (for instance 25,50 and 100).

Equilibration time, averages and fluctuations After having determined the equilibrium time and disregarding the samples for $t < \tau_{eq}$ estimate the ensemble averages of the magnetisation per spin, the energy per spin, and the corresponding fluctuations (specific heat and magnetic susceptibility).

5.2 Exercise

Integrated correlation time and critical slowing-down Estimate the autocorrelation time of the magnetisation and the energy for the MC simulations proposed above and estimate the errors accordingly.

Finite-size analysis and estimates of the critical exponents By following the procedure sketched in section 2.9 and in the lecture perform a finite size scaling analysis of the specific heat, the magnetisation, and the magnetic susceptibility for the 2D Ising model simulated above. Provide a first estimate of the γ and β exponents.

6 Advanced simulations of a 2D Ising model

6.1 Exercise: Wolff cluster algorithm

Implement the Wolff cluster algorithm for the simulation of a 2D Ising model, with periodic boundary conditions.

Cluster size statistics By assuming $k_B = 1$ and $J = 1$, simulate the 2D Ising model ($L = 50$) for different temperatures: the critical temperature $T_c = \frac{2}{\ln\left(1+\sqrt{2}\right)}$, a high temperature $T_h = 2T_c$, and a low temperaturee $T_l = T_c/2$. Collect the cluster sizes of the Wolff algorithm and plot their histograms for the three temperatures. What can one note?

Autocorrelation time For some values of L, compute the autocorrelation time τ at T_c of the magnetization time series for (a) the single-spin flip algorithm, and (b) the Wolff algorithm. Plot them in log-log scale vs L. Do they scale with L as expected?

6.2 Exercise: Multiple Markov chains

Implement multiple Markov chains for the Ising model. Check if the energy distributions of adjacent chains are overlapped. Record the swapping rate between chains. Compare the autocorrelation times of the chains when the swapping is allowed and when it is not (thus making the Markov chains effectively single ones).

7 Continuous time Markov processes, Gillespie algorithm

Implement a flexible base for the Gillespie algorithm so that the following models can be simulated by some simple tweaking.

7.1 Exercise: Lotka-Volterra

Run some simulations of the Lotka-Volterra model with the Gillespie algorithm and the parameters $k_1 = 3$, $k_2 = 1/100$, $k_3 = 5\ s^{-1}$. Start from different initial conditions, either close or far from $\mathcal{C}^*$. Do the predators become extinct in some cases? What happens to the prey in that case? Which variation in the parameters can induce or reduce the chance of this extinction?

7.2 Exercise: Brusselator

Run some simulations of the Brussellator model with the Gillespie algorithm, using $a = 2, b = 5$ and for different volume sizes: $\Omega = 10^2, 10^3, 10^4$. What can one note by varying Ω?

8 Off-lattice simulations: basics

8.1 Exercise: reduced units

Typical sets of parameters for Argon and Krypton are $\sigma_{Ar} = 3.41\mathring{A}$, $\sigma_{Kr} = 3.38\mathring{A}$ for their typical size and $\epsilon_{Ar}/k_B = 119.8K$ and $\epsilon_{Kr}/k_B = 164.0K$.

- At the reduced temperature $T^* = 2$, what is the temperature of Argon and Kelvin?
- A typical value of the integration time step for MD is $\Delta t = 0.001\tau$. Convert it into SI units for Argon and Krypton.
- Compute the expression for the friction coefficient and the dynamical viscosity in reduced units.

8.2 Exercise: off-lattice Monte Carlo

Write a code to simulate a Monte Carlo off-lattice in 3D. A Monte Carlo sweep will consist of N trial moves, where N is the number of particles in your system. For each trial move:

1. Select a particle at random
2. Propose a displacement in each direction. The maximum displacement should be set as a parameter d_{max}.
3. Compute the energy of the system before the displacement.
4. Displace the particle and compute the energy of the system after the displacement
5. Accept or reject according to the Metropolis rule.

Implement periodic boundary conditions. (*Note:* this exercise is just a warm up for the next ones. We suggest to write the code in such a way it can be expanded fairly easily.)

8.3 Exercise: Off lattice Monte Carlo of Hard Spheres

The Hard Sphere model is a paradigmatic model in Soft Matter (despite the naming would not suggest so). The interaction energy between two hard spheres is zero if the separation distance is larger than the diameter of the particle σ and infinite otherwise. For simplicity set σ =1 as the unit of length.
In practice, in such a case one can simplify the Metropolis acceptance rule as follows:

1. reject every displacement that brings any two particles closer than σ – call it an *overlap*. For convenience, assign a very large energy to the configuration if an overlap is present, so that it can be plotted more easily.
2. accept every displacement that keeps every pair of particles at a distance larger than σ or that removes an overlap.

An acceptable state for a Hard Sphere system has zero energy and is homogeneously distributed in the simulation box. The first condition is easily checked; for the second, one can either look at the density along the different axis or at the radial distribution function.
For a system of N =100 particles:

- Starting from random initial conditions (i.e. generate the initial coordinates at random) test the performance of the code for different values of d_{max} between 0.01 σ and 1 σ (consider at least 5 values) at different values of the number density $\rho = N/V =$ 0.05, 0.3, 0.5, 1. Perform an average over at least 10 realizations. Discuss what happens at the acceptance ratio and at the energy as a function of d_{max} upon varying the density.
- Perform the same test, this time starting from a simple cubic crystal with a primitive cell of fixed length σ.

8.4 Exercise: Off lattice Monte Carlo of Lennard Jones particles

The Lennard-Jones interaction is another paradigmatic interaction potential, often used to implement "self-avoidance" in MD simulations or as a paradigmatic example of gas-liquid phase separation. It reads

$$V_{\mathrm{LJ}}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] & \text{for } r < \sigma_{cut} \\ 0 & \text{for } r \geq \sigma_{cut} \end{cases} \tag{4.19}$$

where σ =1, ϵ =1 are the units of length and energy and σ_{cut} is the so-called cut-off length and is set, for this exercise, to half the box size. Beyond this cut-off, we introduce two tail corrections: one for the energy (per particle)

$$u^{tail} = \frac{8}{3}\pi\rho \left[\frac{1}{3} \left(\frac{\sigma}{\sigma_{cut}} \right)^{9} - \left(\frac{\sigma}{\sigma_{cut}} \right)^{3} \right] \tag{4.20}$$

and one for the pressure

$$P^{tail} = \frac{16}{3}\pi\rho^{2} \left[\frac{2}{3} \left(\frac{\sigma}{\sigma_{cut}} \right)^{9} - \left(\frac{\sigma}{\sigma_{cut}} \right)^{3} \right] \tag{4.21}$$

Perform two sets of simulations, one at reduced temperature T^* =2 (above the critical temperature) and one at T^* =0.9 (well below the critical temperature) an compute, for both cases, the equation of state in the pressure-density plane. Compare the results with the equation of state for the two temperature (data shared in Google Drive).

9 Integration schemes

9.1 Exercise: Harmonic Oscillators

Symplectic vs. non-symplectic integrators (credit: Prof. E. Carlon)

Compare the performance of two MD integration schemes for a one-dimensional harmonic oscillator. The Hamilton's equations of motion are:

$$\begin{cases} \dot{p} &= -\frac{\partial H}{\partial x} &= -kx \\ \dot{x} &= \frac{\partial H}{\partial p} &= p/m \end{cases} \tag{4.22}$$

where the Hamiltonian is given by

$$H = \frac{p^2}{2m} + \frac{kx^2}{2} \tag{4.23}$$

Set for convenience $k = m = 1$.
The first integrator (Euler integrator) we consider is

$$\begin{cases} p(t+\Delta t) = p(t) - x(t)\Delta t \\ x(t+\Delta t) = x(t) + p(t)\Delta t \end{cases} \tag{4.24}$$

The second integrator is also first order, but reads:

$$\begin{cases} p(t+\Delta t) = p(t) - x(t)\Delta t \\ x(t+\Delta t) = x(t) + p(t+\Delta t)\Delta t \end{cases} \tag{4.25}$$

Note that there is only a slight difference between the two.

a) Express Eqs. (4.24) and (4.25) in matrix form

$$\begin{pmatrix} x \\ p \end{pmatrix}_{t+\Delta t} = M \begin{pmatrix} x \\ p \end{pmatrix}_t \tag{4.26}$$

and show that for Eq. (4.24) $\det(M) > 1$ while for Eq. (4.25) $\det(M) = 1$. What does this tells us about the two algorithms and why?

Symplectic integrators do not strictly conserve the Hamiltonian H, but they conserve a so-called *shadow*-Hamiltonian H', which differs from H by terms of order Δt^k. For this reason they do not suffer from long time drift as non-symplectic integrators. Symplectic integrators are also volume preserving. The velocity Verlet scheme is a symplectic integrator (and it is of order $k = 2$). Eq. (4.25) defines the so-called Euler symplectic integrator of order $k = 1$.

b) Show analytically that the symplectic integrator defined by Eq. (4.25) has the following constant of motion (shadow Hamiltonian)

$$H' = H - \frac{px}{2}\Delta t \tag{4.27}$$

c) Take $\Delta t = 10^{-3}$ and $\Delta t = 10^{-2}$ with initial conditions $x(0) = 1$, $p(0) = 0$. and plot the solutions of Eqs. (4.24) and (4.25) up to time $T = 10$. Compare the relative errors of the two integration schemes to the exact solution of Eq. (4.22). Which of the two integrators is more accurate?

d) For the same values of the parameters given above plot the value of H as a function of t up to time $T = 10$. Plot H' as well for the symplectic integrator. Which of the two integrators has a long time drift in the energy estimate?

9.2 Exercise: Algorithms

Implement the Velocity Verlet algorithm and another one between: i) Verlet algorithm ii) Beeman algorithm iii) Predictor-corrector algorithm.

9.3 Exercise: The harmonic oscillator #2

$$\begin{aligned} \frac{dq}{dt} &= p, \\ \frac{dp}{dt} &= -\omega^2 q. \end{aligned} \tag{4.28}$$

The exact solution of $p(t)$ vs $\omega q(t)$ we get a circular orbit in phase that rotates by an amount of $\omega\Delta t$ at every time step. Considering this system, compare the two algorithms implemented above in terms of i) energy conservation, plotting $(E(t) - E_0)/E_0$ vs t, E_0 being the initial total energy ii) discrepancy with the analytical solution as a function of time. Verify that the Velocity Verlet is stable (i.e. it follows the analytical solution) for $\omega\Delta t < 2$.

10 Interaction potentials & thermostats

10.1 Exercise: Canonical fluctuations

Show that the fluctuations of the temperature of the system, as defined in class, in the canonical ensemble are

$$\frac{\sigma^2_{T_K}}{\langle T_K \rangle^2} = \frac{\langle T_K^2 \rangle - \langle T_K \rangle^2}{\langle T_K \rangle^2} = \frac{2}{3N} \tag{4.29}$$

10.2 Exercise: Lennard-Jones fluid in the microcanonical ensemble

Simulate N particles of mass $m = 1$ that are confined to move within a cubic box of length L (with periodic boundary conditions). The particles interact with each other through a Lennard-Jones (LJ) potential

$$V_{LJ}(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right) \tag{4.30}$$

where σ =1 and ϵ =1. Choose $L = 10\sigma$ and $\rho = N/V = 0.2\sigma^{-3}$. Integrate the equations of motion with the Velocity Verlet algorithm. (This exercise can be carried on with LAMMPS).

- Generate a suitable, well equilibrated initial condition. Choose one of the two strategies introduced in one of the previous exercise sessions. Draw the initial velocity distribution from the equilibrium (Maxwell-Boltzmann) distribution at $T^* = 1$, enforcing the total momentum to zero.
- Check the effect of the cut-off radius: perform different simulations, increasing the cut-off from $r_c = 2^{1/6}\sigma$ to $r_c = 4\sigma$ with steps $\Delta r_c = 0.2\sigma$ (round the numbers to the first decimal place after the first one). After equilibration (if needed), compute the radial distribution function to compare the different cases.

Optional Do not enforce the initial momentum. Pick two extreme cases $r_c = 2^{1/6}\sigma$ and $r_c = 4\sigma$ and discuss what happens.

Pick one between the following two exercises:

10.3 Exercise

A

Lennard-Jones fluid with thermostats. Simulate again the same LJ system as in the previous exercise, this time with thermostatting. Among the different choices

- Velocity rescaling
- Berendsen thermostat
- Andersen thermostat
- Nose-Hoover thermostat (Note: this can be done in LAMMPS)

pick two, a non-canonical and a canonical thermostat. Fix the reference temperature of the heath bath $T^* = 2$. Integrate the equations of motion with the Velocity Verlet algorithm.

- Compute the kinetic energy and verify that, in both cases, the average is consistent with the equipartition theorem $\langle E_K \rangle = 3/2\, N k_B T$ upon varying the number of particles in the system (keeping the box size fixed); keep $\rho \leq 0.2$.
- Check that the fluctuations of the temperature are consistent/not consistent with the canonical ensemble upon varying the number of particles in the system as above.

Optional From the same simulations, compute the pressure and compare the results with the first correction of the virial expansion $P = \rho k_B T + k_B T b_2 \rho^2$ with $b_2 \simeq -0.772$ for $T^* = 2$.

B

Ideal gas of dumbbells: Consider a system made of N =100 non-interacting dumbbells, each one made of two particles, held together by an harmonic spring with rest distance $r_0 = 1$ (r_0 sets the unit of length). Set, for simplicity, a box $L = 10$ units with periodic boundary conditions. Set the dumbbells initially at random positions in the box; each dumbbell should be at its rest length. Set the initial velocities as in the first exercise (Remember! Each dumbbell is in practice a different system!). Integrate the equations of motion with the Velocity Verlet algorithm. Among the different choices

- Velocity rescaling
- Berendsen thermostat
- Andersen thermostat
- Nose-Hoover thermostat (Note: this can be done in LAMMPS)

pick two, a non-canonical and a canonical thermostat. Fix the reference temperature of the heath bath $T^* = 2$.

- Compute the kinetic energy and verify that the average is consistent with the equipartition theorem $\langle E_K \rangle = 3/2\, N k_B T$.
- Check that the fluctuations of the temperature are consistent/not consistent with the canonical ensemble.
- Check the dyamics of the system in the two cases, by computing the Mean Square Displacement of the dumbbells. Discuss what happens.

optional Do not fix the initial momentum to zero. Discuss what happens.

11 Langevin and Brownian Dynamics

11.1 Exercise: On the validity of the Langevin approach

- The Langevin approach is based on the assumption that the time scale associated with the fluctuations of the heat bath is much smaller than the time scales of the dynamics we are interested in. The correlation time of water molecules is of the order of picoseconds: take that as the time scale of the fluctuations τ_{coll}. Suppose to be strict and to impose that the time step of your algorithm should be at least 10 times larger than τ_{coll}. Given $\Delta t = 10^{-2} - 10^{-3}\tau$ provide an estimation of the minimum size of the object, for which the Langevin description is acceptable. (*Hint*: The energy scale is always the thermal energy at room temperature; for simplicity, the object has roughly the same density as water; also, the object is spherical.)

- In the overdamped limit, the diffusion scale becomes the relevant time scale. Using the Stokes-Einstein formula, estimate the time scale of a particle of diameter $\sigma = 10^{-8}m$ to diffuse in water over a distance equal to its own diameter. Is this time scale compatible with the requirement of the Langevin/Brownian description?

- Conversely, show that, above $\sigma = 5\mu m$, Brownian motion becomes negligible. Which other force becomes relevant?

11.2 Exercise: Simple Brownian motion

Consider an isolated particle (or an "ideal gas" of non interacting Brownian particles). Set $m = 1$, $\sigma = 1$ and $\epsilon = 1$ as units of mass, length, energy. Set $L = 10\sigma$ and apply periodic boundary conditions. Choose initial conditions as you prefer. Simulate this system in the overdamped limit (first order integrator) and in the "underdamped" limit (Stochastic Velocity Verlet or with the second order integrator).

- Compute the mean square displacement and discuss what happens upon varying the temperature ($0.1< T^* <2$, $\gamma = 1\tau^{-1}$) and the friction coefficient ($0.1< \gamma\tau <100$, $T^* = 1$). Pick 5-10 values in each case. Compare the results with the theory.

- **[Optional]** In the underdamped case, compute the diffusion coefficient via the Green-Kubo relation.

11.3 Exercise

Pick one between the following two exercises:

A

Overdamped colloid in an harmonic trap: consider a single overdamped particle (or, again, an ideal gas of non-interacting overdamped particles) in an harmonic trap, centred in a certain point of the box $\vec{r}_0$ (for simplicity, choose the origin of the reference frame or the centre of the box).

$$V(r) = \frac{1}{2}K(\vec{r} - \vec{r}_0)^2 \tag{4.31}$$

Set $m = 1$, $\sigma = 1$ and $\epsilon = 1$ as units of mass, length, energy. Set 20σ and apply periodic boundary conditions; in this case, consider the system in 2D. Fix the initial conditions as i) particles always start at a fixed distance from the trap $r(0)$ ii) velocities are drawn from the equilibrium distribution.

- Compute the average and the variance of the position along one axis as a function of $0.1 < K\sigma^2/\epsilon < 10$, $0.1 < \gamma\tau < 100$, 0.1< T^* <2 (Note: when varying one quantity, keep the others fixed to unitary value)
- Compute the time correlation of the distance (along one axis) between the particle and the centre of the probe in equilibrium and discuss the result.
- Set another harmonic trap at a distance 2σ from the first one (shift it along one of the cartesian axes). Fix $\gamma = 1$, $T^* = 1$ and $K = 1$. Estimate the average time it takes the particle to jump in the the other trap (i.e. the particle is closer to the second trap than to the first), as a function of the initial position, that should be varied from the centre of the first trap to the mid-point between the two. How does the variance of such time behave? (Note: we want here the First Passage Time. The minimum time possible is the diffusion time!)

B

Langevin description of a Gaussian polymer: a Gaussian polymer is a set of particles (beads) connected in pairs by harmonic springs. In particular, given N beads, any two neighbouring beads i and $i+1$ of coordinates $\vec{r}_i$ and $\vec{r}_{i+1}$ ($i = 1, N-1$) are connected by

$$V(r) = \frac{1}{2}K(r - r_0)^2 \tag{4.32}$$

where $r = \sqrt{(\vec{r}_{i+1} - \vec{r}_i)^2}$ is the distance between them and r_0 is the preferred length. There is no other interaction between the beads. Set $m = 1$, $\sigma = 1$ and $\epsilon = 1$ as units of mass, length, energy. Set $L = 20\sigma$ and apply periodic boundary conditions. Simulate Langevin or Brownian dynamics in 3D, setting $\gamma = 1$, $T^* = 1$ and $k = 10\epsilon/\sigma$. A polymer is usually characterized, at the simplest level, by its (average) square gyration radius

$$\langle R_g^2 \rangle = \langle \frac{1}{N} \sum_i^N (\vec{r}_i - \vec{r}_{com})^2 \rangle \tag{4.33}$$

where $\vec{r}_{com}$ is the position of the centre of mass and the average is an ensemble average.

- For an ensemble of M=10 non-interacting chains of $N = 20$ beads (set $r_0 = 1\sigma$), discuss what happens to the gyration radius as a function of time when starting from two different initial conditions a) beads on a straight line b) a random walk. (Note: simulate until R_g^2 is fluctuating around a constant value).
- Pick one between a) and b) as initial conditions. Keep $M = 10$ and $N = 20$. Discuss what happens to the gyration radius at equilibrium, upon varying r_0 in the range $0.1\sigma < r_0 < 10\sigma$ (pick at least 5 values). Does it make sense to do so? Discuss.
- Pick one between a) and b) as initial conditions. Set $M = 20$ and set $r_0 = 1\sigma$. Verify that the *scaling* law $R_g^2 \propto N$ is verified, simulating polymers between $N = 20$ and $N = 500$ (pick at least 8 values). [Notes: 1. The scaling law does not apply for polymers below $N \sim 50$ monomers 2. Note that is a bad practice to simulate a polymer in a box whose linear size is comparable or smaller with its gyration radius, because the polymer can interact with itself through the periodic boundaries; in this case there is no interaction and we can make an exception 3. The ensemble average of the gyration radius oscillates over time and the period of these oscillations increases upon increasing N, which makes simulating larger polymers even more challenging]

12 Reweighting techniques

12.1 Exercise: Change of measure

For a canonical distribution π at inverse temperature β, prove the second equality of

$$\langle O \rangle_\pi = \left\langle O \frac{\pi}{g} \right\rangle_g = \frac{\left\langle O \frac{e^{-\beta E}}{g} \right\rangle_g}{\left\langle \frac{e^{-\beta E}}{g} \right\rangle_g} \tag{4.34}$$

where g is another probability distribution function.

12.2 Exercise: Single Histogram Method

Choose a system, for example, the two-dimensional Ising model, and run $K \geq 3$ simulations at different temperatures, collecting data on the energy of samples.

Apply the single histogram method to extrapolate the average internal energy $U(\beta) = \langle E \rangle_\beta$ from data at one β_i to a range of β covering the selected $\beta_1, \ldots, \beta_K$ (i.e., here ignore the data from $\beta_k \neq \beta_i$). Comment on the overlap between this prediction and the usual evaluation of the internal energy $U(\beta_k)$ obtained directly from data at β_k.

Is the extrapolated U getting worse when β departs too much from β_i?

How does the prediction $U(\beta)$ change with the β_i?

12.3 Exercise: Multiple Histogram Method (MHM)

Following the previous point, now obtain $U(\beta)$ from the MHM based on *all* β's data and comment on the new result.

Then, use the MHM to compute the specific heat

$$C(\beta) = \frac{1}{N\beta^2}[\langle E^2 \rangle_\beta - \langle E \rangle_\beta^2]$$

(note the normalization by the number N of degrees of freedom) and for at least three system sizes. Is the location β_N of $C(\beta)$'s maximum approaching a critical inverse temperature β_c for increasing system size?

When counting data in histograms $N_i(E)$ and total measurements M_i, do you rescale them by the autocorrelation times τ_i of stored data?

12.4 Optional Exercise: Umbrella Sampling

Implement a simple example showcasing a good usage of umbrella sampling.

assignment: understand what's going on in this code, spot the most important points and do requested simulations

13 Langevin simulation of many particles

This exercise is based on the C code provided in the previous lesson.

MSD <delta x^2> \sim t^2 || t << tau
D=T/gamma =!= D_eff (ACTIVE)

13.1 Exercise: Cell list

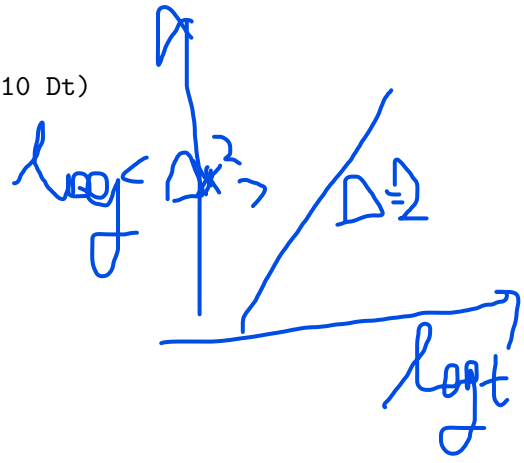
Comment on the two implementations of the cell list, namely the version for particle 0 and the version for smaller particles. Which is the best algorithm?

the t^2 can be due to inertia
or viscosity or active fluid

13.2 Exercise: Active matter

We aim to use the N small particles to implement $N/2$ "active dumbbells", each one representing a bacterium with propulsion. Each one is composed of particles i and $i+1$. They are kept apart by a harmonic spring of rest length $\Lambda = 1/2$. Moreover, particles i and $i+1$ feel a propulsive force $\vec{f}$ oriented as the vector $\vec{r}_i \to \vec{r}_{i+1}$, and of magnitude f. Implement this system.

To study the active Matter and diffusion of the probe, remove the harmonic trap that would keep the probe confined and study the diffusion of the probe in the bath of $N/2$ active dumbbells. Focus on the mean square displacement as a function of time. Study it for different values of f, starting from $f = 0$ (equilibrium). How does the probe's mean square displacement change with f?



asimtotically there will be normal distribution

Plausible or mandatory $(*)$ parameters

```
nstep_save=0; // saving configs if >0 (e.g. =10 saves every 10 Dt)
N=2000;       // nr of small particles
Lp=2;         // length of each dumbbell
box[0]=40;    // box size, x
box[1]=40;    // box size, y
T=1;          // temperature (kB=1)
v_trap_ini=...; // smallest velocity of the trap. NOT USED
Nv=...;              // number of velocities. NOT USED
v_per_decade=...;    // velocities per decade. NOT USED
(*) k_trap=0; // stiffness of the trap
k_pol=10;     // stiffness of the polymer bonds
(*) R=0.125;  // "radius" of each particle
eps=10;       // repulsive energy of particles
R0=1.25;      // "radius" of the probe
eps0=20;      // repulsive energy of the probe
dt=1e-3;      // integration time step
tt=10000;     // total time of the simulation

---ADD---
Lambda=0.5
f_active=....
```

To generate an mp4 video from the folder containing the png frames, a command might look like:

```
ffmpeg -r 10 -f image2 -pattern_type sequence -start_number 100001 -i fr_%06d.png -s 500x500 video.mp4
```

the idea is to always use the previous configuration as the initial state for the next one

name of the files as an indicator of the force: files -> 0 <- fa