Computer Simulations

2^{nd} exam

Summer term 2025
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Theory exam

October 9, 2025

Available time: 1 hour

Write your name and student number on every sheet you submit.

1. Optimization

We want to find the minimum of the function

$$f(x) = x^4 - 2x^2 + hx.$$

where $h \neq 0$ is a real-valued constant.

(a) Explain whether a deterministic method, such as steepest descent, is guaranteed to find the global minimum, depending on h.

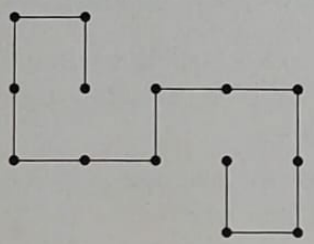
(b) Explain the steps involved in an optimization by simulated annealing.

2. Monte Carlo simulations

We perform a Monte Carlo simulation of a polymer consisting of N monomers in two-dimensional space. Monomers can only exist on the nodes of a rectangular grid and the distance between monomers is always equal to the distance a between the grid points. We use so-called reptation moves, an example of which is shown in the scheme below.

Every move, one end is selected at random and one monomer is removed from that end. At the other end, a monomer is added in a random direction. The move is only accepted if the added monomer lands on an empty grid point.

(a) Explain whether the simulation scheme is ergodic for large N based on the figure below.



The vector connecting the first and the last monomers of the polymer is denoted the end-to-end vector $\boldsymbol{R} = (R_x, R_y)$. Assuming that we have designed an ergodic scheme to generate a total of M accepted configurations, we can generate the vectors $\boldsymbol{R}^{(i)}$ for $i = 1 \ldots M$.

(b) Write down the equation for the ensemble average $\langle R_x \rangle$ calculated from the M configurations.

The ensemble average $\langle R_x \rangle$ can be written generally as

$$\langle R_x \rangle = \frac{\sum_{i=1}^{\infty} R_x^{(i)} \exp(-\beta E^{(i)})}{\sum_{i=1}^{\infty} \exp(-\beta E^{(i)})},$$

with β being the inverse thermal energy.

(c) What is the function $E^{(i)}$ corresponding to the acceptance criteria of the reptation algorithm described above?

When an external force f_x, pointing in x direction, is applied to the ends of the polymer, the energy of each configuration is given by

$$E_f^{(i)} = E^{(i)} - f_x R_x^{(i)}.$$

Due to the force, the ensemble average extension in x direction increases by $\langle \Delta R_x \rangle = \frac{1}{k} f_x$. We are interested in calculating the spring constant k.

(d) Write down an expression for k in terms of a derivative of $\langle \Delta R_x \rangle$.

(e) Show that the spring constant can be calculated from

$$\frac{1}{k} = \beta \left[\langle R_x^2 \rangle - \langle R_x \rangle^2 \right].$$

3. **Molecular dynamics simulations**

Consider a molecular dynamics simulation with N particles. Because we are interested in the velocities $\boldsymbol{v}$, we use the velocity Verlet algorithm,

$$\begin{aligned} \boldsymbol{r}(t+dt) &= \boldsymbol{r}(t) + \boldsymbol{v}(t)dt + \tfrac{1}{2}\boldsymbol{a}(t)dt^2 \\ \boldsymbol{v}(t+dt) &= \boldsymbol{v}(t) + \tfrac{1}{2}(\boldsymbol{a}(t) + \boldsymbol{a}(t+dt))dt \end{aligned} \tag{1}$$

with $\boldsymbol{r}$ and $\boldsymbol{a}$ being the positions and accelerations, respectively, and dt being the time step.

(a) Show that Eq. (1) is time reversible.

At time step t_j, particle i has an absolute velocity $v_i(t_j) = |\boldsymbol{v}_i(t_j)|$. Cutting the observed maximum velocity v_{max} into $n_b = v_{max}/\Delta v$ intervals, we estimate from the simulation that the probability that a particle has a velocity between some value v and $v + \Delta v$ equals $p \pm \sigma_p$, with σ_p being the standard deviation.

(b) Explain how σ_p is expected to change when the number of particles N in the simulation is doubled. You may assume that N is large compared to the number of intervals n_b.

(c) After T time steps, the average velocity is given as $\langle v \rangle \pm \sigma_v$. The standard deviation is calculated from

$$\sigma_v^2 = \frac{1}{NT}\left[\left(\frac{1}{NT}\sum_{i=1}^{N}\sum_{j=1}^{T} v_i(t_j)^2\right) - \left(\frac{1}{NT}\sum_{i=1}^{N}\sum_{j=1}^{T} v_i(t_j)\right)^2\right]$$

Explain why this equation will not provide a good estimate of the standard deviation in a molecular dynamics simulation and describe one possible procedure that can be used to improve the estimate.