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FB Mathematik und Informatik

Computational Molecular Physics **Winter 2017/18**

Exam **5 February 2018**

For one of the following two problems, a detailed written solution must be handed in. The oral exam will cover the solutions to both problems. Every question needs to be answered by a piece of text with accompanying figures, every figure shall have a caption and be referenced in the text. Methods and algorithms used shall be outlined briefly. Pay attention to physical dimensions and units, and give error estimates where possible.

Problem 1 *Conformational dynamics of a small molecule*

The file `butane.xyz` contains the trajectory of the small molecule butane as Cartesian coordinates (in Ångstrøm). For each frame written, the first line is the number of atoms, the second line is a title and the following lines contain the set of coordinates. These data have been generated by a molecular dynamics simulation with a time step of 1 fs and were saved every time step. A thermostat has been applied so as to control temperature and to generate a NVT ensemble.

a) Read in the trajectory and compute and plot the root mean square deviation as a function of time.

b) Compute the kinetic energy of the system for each, but the first time step, from the velocities of the atoms. The velocities can be obtained as central differences of the positions. Use these data to compute the instantaneous temperature as a function of time. What is the average temperature? How large are the fluctuations in the temperature? Comment on your results.

c) From the trajectory of Cartesian coordinates, compute the dihedral angle of the four carbon atoms (C1, C2, C3, and C4) as a function of time. Use a reasonable discretisation and compute and plot a histogramme of the dihedral angle. Compute and plot the relative free energy as a function of C1-C2-C3-C4 dihedral angle.

d) The histogramme or free energy plot of the dihedral angle suggests a coarse-grained discretisation into a few states based on the dihedral angle value. How many? Assign each time step to one of those states. Set up a transition matrix from counting transitions between those states. Which processes describe the dominant dynamics of the butane's C1-C2-C3-C4 dihedral angle and what are the associated time scales? How does the stationary distribution obtained from the transition matrix compare to the probabilities contained in the histogramme?

e) Compute the time autocorrelation function (acf) for each of the discrete, coarse states. Plot the acf. Estimate time scales (decay times) from the acf by a fit to an exponential function. How do these time scales compare to those obtained from the transition matrix? Discuss.

f) Extract the time series of the C2–C3 distances and the C2-H21 distances from the trajectory and plot them. Compute the linear (Pearson) correlation between the two distances and between each of the distance and the C1-C2-C3-C4 dihedral angle.

Problem 2 *Dynamics in an energy landscape*

Consider the dynamics of a single mass m in a one-dimensional, time-independent energy landscape. The mass is coupled to a heat bath at temperature $T = 4\,\mathrm{pN\,nm}$. Recordings of the random path $X(t)$ are given in the ASCII data files `landscape.dat.bz2` and `landscape-long.dat.bz2`; each column refers to an independent recording. The first file uses a sampling interval of $\Delta t = 1\,\mathrm{ns}$, while the second one has $\Delta t = 100\,\mathrm{ns}$ as specified in the file headers; positions are quoted in nanometres. For each question, use the resolution which is more appropriate, or combine both files.

The following analyses shall be performed:

a) Reconstruct the potential landscape $U(x)$ from the mean density $\rho(x) = \langle \delta(x - X(t)) \rangle$ in equilibrium. Describe your result by a polynomial fit of order 6.

b) Perform a clustering of the trajectories into metastable sets using, e.g., the k-means algorithm. Derive a Markov state model for the observed process by constructing the transition matrix and estimate the implied time scales of the model. Check the robustness of your results by carrying out the analysis for a sequence of lag times.

c) Find the velocity autocorrelation function $Z(t)$ from the statistics of the increments and discuss its behaviour at short times. Determine the thermal velocity $v_{\mathrm{th}} = \sqrt{k_B T/m}$, the mass m, and the rate γ of momentum relaxation. Estimate the integral $\int_0^\infty Z(t)\,\mathrm{d}t$ and explain your result.

d) Calculate the mean-square displacement $\delta x^2(t) := \langle [X(t) - X(0)]^2 \rangle$ and discuss the limiting behaviours for $t \to 0$ and $t \to \infty$ using a double-logarithmic representation. Describe additional features of $\delta x^2(t)$ observed in a plot of $\delta x^2(t)/t$ vs. $\log(t)$. Which dynamic processes do you expect from the potential obtained in question a)?

e) Compute the power spectral density $S(\omega)$ of the position, either directly or indirectly via the increments. Discuss the observed and expected behaviour for small and large frequencies, $\omega \to 0$ and $\omega \to \infty$. Determine the frequency ω_0 of maximum dissipation, i.e., where $\omega S(\omega)$ becomes maximal.

Note: The above text contains hyperlinks to the data files. The URLs are as follows:

`http://userpage.fu-berlin.de/pimhof/butane.xyz`
`http://ftp.imp.fu-berlin.de/pub/hoefling/landscape.dat.bz2`
`http://ftp.imp.fu-berlin.de/pub/hoefling/landscape-long.dat.bz2`

Due date: ***28 February 2018***