Problem set 10: Computational Molecular Physics and Methods of Molecular Simulations

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1 Metastable processes and transition matrices

- Name at least two properties that are valid for all transition matrix.
- Can a transition matrix have complex eigenvalues?
- Just by inspection, are the following matrices metastable or not? Give a detailed explanation, why you come to that conclusion. What do you expect their eigenvalues and eigenvectors to look like?

$$P_1 = \begin{pmatrix} 0 & 0.2 & 0.8 & 0 & 0 \\ 0.01 & 0 & 0.99 & 0 & 0 \\ 0 & 0.1 & 0.8 & 0 & 0 \\ 0 & 0 & 0 & 0.9 & 0.1 \\ 0 & 0 & 0 & 0.3 & 0.7 \end{pmatrix}$$

$$P_2 = \begin{pmatrix} 0.9 & 0.1 & 0 & 0 & 0 \\ 0.2 & 0.8 & 0 & 0 & 0 \\ 0 & 0.1 & 0.8 & 0.1 & 0 \\ 0 & 0 & 0.01 & 0.89 & 0.1 \\ 0 & 0 & 0 & 0.3 & 0.7 \end{pmatrix}$$

$$P_3 = \begin{pmatrix} 0.9 & 0.1 & 0 & 0 & 0 \\ 0.05 & 0 & 0.95 & 0 & 0 \\ 0 & 0.1 & 0.8 & 0.1 & 0 \\ 0 & 0 & 0 & 0.9 & 0.1 \\ 0 & 0 & 0 & 0.3 & 0.7 \end{pmatrix}$$

- Work out whether the following transition matrix is metastable:

$$P(\tau = 1) = \begin{pmatrix} 0.99 & 0.006 & 0.004 \\ 0.31 & 0.37 & 0.32 \\ 0.002 & 0.008 & 0.99 \end{pmatrix}$$

  How do you expect the spectrum of the matrix to change, if P was generated at a lagtime $\tau = 10$ instead of $\tau = 1$.

2 Detailed Balance

A Markov process is reversible if the detailed balance condition $\pi_i p_{ij} = \pi_j p_{ji}$ is satisfied for all pairs of states $i, j \in S$. Show that detailed balance implies

(i) For every cycle $\gamma = (x_1, x_2, \ldots, x_n)$ with $x_1, \ldots, x_n \in S$, it holds that

$$p_{x_1 x_2} p_{x_2 x_3} \cdots p_{x_{n-1} x_n} p_{x_n x_1} = p_{x_1 x_n} p_{x_n x_{n-1}} \cdots p_{x_3 x_2} p_{x_2 x_1},$$

in other words: The probability to go clockwise through γ equals the probability to go counterclockwise.

(ii) $\langle \cdot, P(\cdot) \rangle_\pi = \langle P(\cdot), \cdot \rangle_\pi$, where the scalar product $\langle \cdot, \cdot \rangle_\pi$ is defined as $\langle u, v \rangle_\pi = \sum_{i \in S} u(i) v(i) \pi(i)$.

3 Markov models and transition matrices

Given a three-state Markov model with transition matrix

$$P = \begin{pmatrix} 0.90 & 0.10 & 0.00 \\ 0.25 & 0.50 & 0.25 \\ 0.00 & 0.20 & 0.80 \end{pmatrix}$$

1. Compute the left and right eigenvectors, the eigenvalues, and the stationary distribution and discuss their interpretation.
2. Compute the slowest rate / timescale.
3. Simulate a time series realizaton for different lengths of your choice. Which length do you consider sufficient to get "good" statistics?
4. Plot this time series as well as the evaluation of this time series in two observables: $\hat{A} = [0, 1, 1]$, $\hat{B} = [0.1, 1, 0.2]$.
5. Normalize A and B as described in the lecture.
6. Compute the autocorrelation functions of the normalized A and B.
7. Estimate the slowest rate as a function of lag time $k * \tau$.
8. Which of the two observables is better?

4 Harmonic oscillator

Given are the position densities of a one-dimensional harmonic oscillator, see the follwing figures

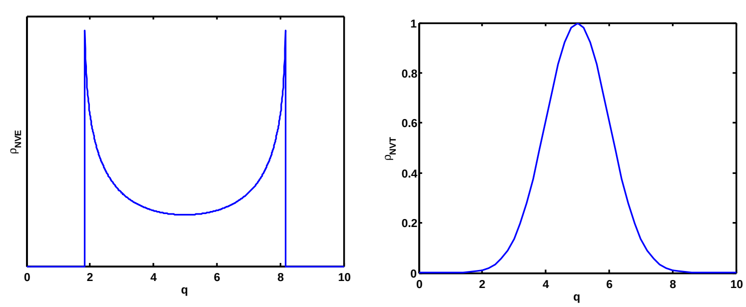

Figure 1: Position densities for different thermodynamic ensembles

- Which of the distributions belongs to an NVE ensemble, which to an NVT ensemble? And how can these two distributions be generated by means of classical trajectories?
- Sketch qualitatively how the corresponding distributions in momentum space and in phase space should look like.