

Project 08

Entropy estimation

Keywords: Free energy calculation, free energy perturbation, thermodynamic integration

Deadline: Please, hand in your report by **Tuesday, 29 July 2014**

1 Introduction

Similar to absolute free energies, the estimation of absolute entropies from MD simulations is not possible, because the associated ensemble averages. However, the estimation of entropy differences is possible. In the lecture, we discussed four methods to estimate entropy differences from MD simulations, two of which relied on a estimation of the free energy difference which then was used to estimate the entropy difference. The other calculated the entropy difference between two states directly by adapting the free energy perturbation method (FEP) and the thermodynamic integration method (TI). (See also Ref. 2.) In this project, you will test and compare these four methods for one-dimensional potential energy functions.

2 Outline of the project

1. Choose two suitable one-dimensional potential energy functions and analytically calculate their entropy difference at temperature T (using the Shannon definition of the entropy) and their free energy difference.
2. Sample the two potentials at three different temperatures: $T - \Delta T$, T , $T + \Delta T$ using the free energy perturbation method and the thermodynamic integration method. Compare the results of the two methods.
3. From these results, calculate entropy differences as

$$\Delta S_{AB} = \frac{\Delta U_{AB} - A_{AB}}{T}$$

and using the finite temperature difference method.

4. Calculate the entropy difference using the TI and the FEP analogue for entropies.
5. Compare and discuss your results.

3 Literature

- Lecture notes and exercises.
- C. Peter, C. Oostenbrink, A. van Dorp, W. F. van Gunsteren "Estimating entropies from molecular dynamics simulations", *J. Chem. Phys.* **120**, p. 2652-2661 (2004).
- Chapters 7 and 10 in: D. Frenkel, B. Smit, "Understanding Molecular Simulation - From Algorithms to Applications", Academic Press, Elsevier (USA) 2002.

Project requirements

- Describe the results of the your project in a report of 5 to 12 pages (font size 11 pt).
- The report should also contain a short description of the theory and the methods. If you implement an algorithm, briefly describe the algorithm.

- Hand in your program along with the report.
- You will present the results of your project in a 20-minute presentation, after which we will have about 10 minutes time for discussion.
- Besides questions which are directly related to the results of the project, the discussion will also cover the theory of the project and the course content which is relevant to the project.
- If you run into problems during the project or have questions, please contact us
 - Bettina Keller, bettina.keller@fu-berlin.de
 - Francesca Vitalini, francesca.vitalini11@gmail.com
- During the lecture hours (Thu, 2.15 - 3.45 pm) one of us will be in the library to answer questions.