

NTNU – Trondheim Norwegian University of Science and Technology

Department of Chemistry

Examination paper for TKJ4205/KJ8902 Molecular Modeling

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Examination date: 2013-12-19 Examination time (from-to): 15.00-19.00 Permitted examination support material: A (All printed and hand-written documents. All calculators)

Other information: 100 points is distributed on four tasks. The numbers in parenthesis indicate the number of points for each subtask.

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TKJ4205/KJ8902 Molecular Modelling Exam 19.12.2013, 15.00-19.00

Norges Teknisk-Naturvitenskapelige Universitet (NTNU)

Code A: All printed and hand-written texts are allowed. All calculators are allowed. Contact: Prof. Per-Olof Åstrand, Dep. of Chemistry, cell phone: 9346 3033 NB: The tasks are not weighted equally. The weight for each task is given in parenthesis after the task number. The weights sum up to 100.

Exercise 1(30)

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In the computational exercises, we do standard "DFT" calculations. Briefly explain and describe the key elements and approximations in the methodology used. (Regard a single point energy calculation, i.e. geometry optimizations or molecular property calculations do not have to be explained).

Exercise 2(10)

Give the definition and a physical interpretation of the electronegativity. How can the electronegativity be used in a force field?

Exercise 3(10)

What is a molecular descriptor and give examples of different types of molecular descriptors? What is a QSPR model and how are molecular descriptors used in a QSPR model? In which research field has QSPR been commonly employed?

See next page for Exercise 4

Exercise 4 (10, 15, 15, 10)

A complex molecule has two stable configurations. This molecule consists of two molecular groups that are rigid, but the distance between these two molecular groups can vary. To a very good approximation this complex molecule can be described by a simple model of a diatomic molecule A - B where the "atoms" A and B refer to the two rigid molecular groups. Based on DFT calculations, the potential energy as function of separation distance d between A and B was obtained (see figure 1). It clearly shows that there are two stable configurations, a contracted state and an extended state.



Figure 1: Intra-molecular potential energy as function of separation distance.

a) You plan to study following properties: The equilibrium constant K between contracted and extended state, the rate constant from one state to the other, the average life-time of each state, the free energy as function of distance d. Which of these properties could be calculated with Molecular Dynamics (MD) and with Monte Carlo (MC) simulations, respectively?

b) Now you want to run the simulation in a solvent in an NVT simulation. Make a sketch of how you think the solvent will change the free energy and discuss it (Draw the free energy of the gas phase situation and draw on top of it the free energy in the solvent, and discuss how the minima in the curve will change). Regard two cases i) both the contracted and the extended states are unpolar; ii) the contracted state is unpolar and the extended state is polar. We can assume that in any case no solvent molecule is able to get in between A and B.

c) You run a long MD simulation at 300 K with a single A - B molecule and 100 solvent molecules. You start from a situation in which the A - B molecule is in the compact state. After many days of simulating this system you have not observed a single transition to the extended state. What are the conclusions and what would you do?

d) You now study this transition at a much higher temperature. At this temperature the transitions occur more frequently and can be studied by long brute force MD trajectories. You want to determine the following time-correlation function

$$C(t) = \frac{\langle \theta(2.9 \text{ \AA} - d(0)) \ \theta(d(t) - 2.9 \text{ \AA}) \rangle}{\langle \theta(2.9 \text{ \AA} - d(0)) \rangle}$$

Here, θ is the Heaviside step-function: $\theta(x) = 1$ if x > 0, $\theta(x) = 0$ if $x \le 0$. The brackets $\langle \ldots \rangle$ denote an NVT ensemble average over the initial conditions (at t = 0). The 2.9 Å is the top of the potential curve in figure 1 and you define any state with a distance d smaller than this value to be compact, and with a distance d larger than this value to be extended.

Except for t being very close to zero, the shape of the correlation function C(t) won't change too much if you choose a slightly different value, e.g 2.7 Å or 3.0 Å. Can you explain why? What can you say about C(t) in the limit $t \to \infty$ in terms of the equilibrium constant?