Freie Universität Berlin
Fachbereich Physik
Prof. Dr. Roland Netz
*http://www.physik.fu-berlin.de/en/einrichtungen/ag/ag-netz/lehre*

Hand in on February 6th 2017 before the lecture

# Advanced Statistical Physics II – Problem Sheet 13

## Problem 1 – **Reaction rate kinetics**

Consider the reactions

$$A + A \xrightarrow{k_2} B \qquad \text{and} \qquad B \xrightarrow{k_1} A + A \tag{1}$$

of two chemical substances $A$ and $B$ that are solvated in water. In the lecture it has been shown that the chemical kinetics equation of these reactions read as

$$\dot{y}(t) = k_2 x^2(t) - k_1 y(t) \tag{2}$$

where $x$ is the concentration of substance $A$ in water, $y$ is the concentration of substance $B$ in water and $k_1$ and $k_2$ are some reaction rates.

a) (2P) Let the state in which there is only substance $A$ present in the solution without substance $B$ be denoted by the concentrations $x = x^\star$ and $y = 0$. Find a relation between $x(t)$ and $y(t)$ for an arbitrary state assuming that no particles can enter or leave the system, such that the mass of both substances together is conserved.

b) (2P) Show that there are two stationary states characterized by the concentrations $y_1$ and $y_2$ of substance $B$. The solutions are

$$y_{1/2} = \frac{x^\star}{2} + \frac{\kappa}{8} \pm \sqrt{\frac{\kappa}{8}\left(\frac{\kappa}{8} + x^\star\right)} = \left(\sqrt{\frac{\kappa}{16} + \frac{x^\star}{2}} \pm \frac{\sqrt{\kappa}}{4}\right)^2 , \tag{3}$$

with $\kappa = k_1/k_2$.

c) (2P) Show that the nonlinear differential equation (2) can be rewritten as

$$\int_{y_0}^{y} \frac{\mathrm{d}y'}{(y' - y_1)(y' - y_2)} = 4k_2 \int_0^t \mathrm{d}t = 4k_2 t \,, \tag{4}$$

where we denote $y(t = 0) = y_0$.

d) (4P) Compute the integral in equation (5) and solve the resulting equation for $y(t)$.
Result:

$$y(t) = y_2 + \frac{y_1 - y_2}{1 - \frac{y_0 - y_1}{y_0 - y_2}\,\mathrm{e}^{4k_2(y_1 - y_2)t}} \,, \tag{5}$$

e) (2P) Take the limit $t \to \infty$. For which initial values $y_0$ do you end up at the stationary state $y_1$, for which in the state $y_2$? What does this tell you about the stationary states $y_1$ and $y_2$?

## Problem 2 – **Master equation**

Consider two states $A$ and $B$.

$$A \xrightarrow{k_2} B \qquad \text{and} \qquad B \xrightarrow{k_1} A \tag{6}$$

where the rate from $A$ to $B$ is given by $k_2$ and from $B$ to $A$ is given by $k_1$.

a) (2P) Write down the Master equation for the probability $p_A(t)$ and $p_B(t)$.

b) (2P) Solve the system of differential equations for $p_A(t)$ and $p_B(t)$ with initial distribution $p_A(t=0) = p_A^0$ and $p_B(t=0) = p_B^0$.

c) (2P) Consider the trajectory $I(t)$, which is defined to be 0 when the system is in state $A$ and 1 when in state $B$: $I = \{0, 1\}$. State $A$ represents for example a folded state of a protein and $B$ represents an unfolded state. Calculate $\langle I(t) \rangle$. How does $\langle I(t) \rangle$ behave for $t \to \infty$?

d) (2P) Calculate $\langle I(t)I(0) \rangle - \langle I^2(t) \rangle$.