Workshop -3d

Physical Chemistry II

Exercises and Homework Set 2

Conceptional Review

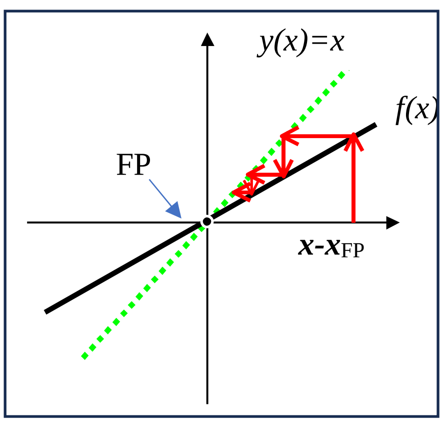
i. Discuss some features of Logistic-Map (LM) dynamics: Why does the character of the iterations change so strongly with the magnitude of the gain/amplification parameter **μ**? Explain the plot of asymptotic intensity I_n vs. μ. What does "bifurcation" or multiple bifurcation mean? What are their relation to "periodic points," points of period *n*?

ii. What is a heuristic meaning of the Lyapunov exponent **λ**? What is the character of LM iterations for **λ=0**?

iii. Why would one expect the autocatalytic reaction $A+B \rightleftarrows B+B$ behave non linearly with respect to the concentrations of the reagents? What do the different lengths of the arrows imply?

iv. Review the method of *partial fraction decomposition* for product functions.

1. Basic Types of Map Behavior Near Fixpoints



Consider a map profile ***f(x)*** to be *linearized* as $x_{n+1} \approx s \cdot x_n + C$ in the vicinity of a fixpoint $x=x_{FP}$. Here, ***s*** is the slope of the map profile function *f(x)* and *C* is a real constant.

a) Determine graphically the behavior of the iterates (trajectories) in the *FP* neighborhoods, for the cases

1) $0 < s < 1$ 2) $-1 < s < 0$

3) $1 < s$ 4) $s < -1$

b) How can the iterative behavior be predicted from the slope *s* of the function $f(x)= s \cdot x$ at fixpoint $x=x_{FP}$?

c) How can the iterative behavior be predicted from the slope *s* of the function $f(x)= s \cdot x + C$ at fixpoint $x=x_{FP}$, for $C \neq 0$?

2. Logistic Map Numerical Evaluation

Modify the provided MS Excel code to model the Logistic Map behavior for the range of input variable $x \in [0,1]$ with several gain parameters μ. Follow approximately 10 iterations.

a) For μ = 2.5 check for initial values $x_0 \approx 0.3$ and $x_0 \approx 0.7$, if and how iterations depend on initial conditions. Plot (in MS Excel) the iterates x_n *vs.* iteration number *n*.

b) For μ = 0.5, check for initial values around $x_0 \approx 0.6$, if and how iterations depend on initial conditions. Plot (in MS Excel) the iterates x_n *vs.* iteration number *n*.

3. Limited Population Growth

Consider the bounded growth of a population described by an effective rate law

$$\dot{x} = \frac{dx}{dt} = r \cdot x \cdot \left(1 - \frac{x}{K}\right); \quad r = const > 0$$

with a constant strength parameter *r*. Let the starting population be $\boldsymbol{x}_0 = \boldsymbol{x}(t=0)$.

a) What is the functional behavior of *x(t)* for the small early populations and what is it in the regime approaching the maximum sustainable population *x=K ?*

b) Explore the time dependent population function

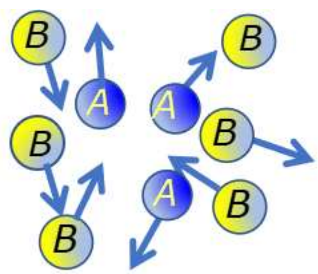
$$x(t) = \frac{K \cdot x_0}{K + x_0 \cdot \left(e^{r \cdot t} - 1\right)} \cdot e^{r \cdot t}$$

by explaining the meanings of x_0 and *K* by the short time and longtime behavior of this function.

c) Is this a population consistent with a rate law such as considered above in a)?

d) Show whether or not the above population function lead to a steady population.

4. Rate and Yield of an Autocatalytic Reaction



Consider the autocatalytic reaction $A + B \rightarrow B + B$ occurring in a reaction vessel with reaction rate constant $\boldsymbol{k}$. Let the time-dependent concentrations $C_A(t)$ and $C_B(t)$ have the initial values $C_A(t=0) = A_0$, $C_B(t=0) = B_0$ at time zero.

a) Write down the differential rate law for $C_B(t)$.

b) Derive the solution $C_B(t)$ of the rate equation for all *t*.

(**Hint:** The **method of partial fractions** is useful for integrating the rate equation.)

c) How does the final yield in B depend on the ratio A(0)/B(0) of the initial concentrations?