Due: Workshop-3d

Physical Chemistry II

Exercises and Homework Set 3

Conceptional and Math Review

A. Stability and equilibrium in chemical reactions, method of variations. Linearity of the derivative operator ***d/dt***.
B. Discussion of computer simulation code for predator-prey dynamics.
C. Cellular automata: Taking account only of the status of nearest neighbors, how many evolution rules are possible for a 1D or 3D CA? How does that number scale when also the next-to-nearest cells are included? What kind of patterns result from discrete or continuous initial conditions?
D. What is a fractal structure? What geometrical properties make them different from other materials? Are fractal structures found in nature?
E. Discuss Euler's formula $\exp\{i\cdot\varpi\cdot t\}=\cos(\varpi t)+i\cdot\sin(\varpi t)$ and its first and second derivatives d/dt. Contrast this behavior with that corresponding to real exponents.
F. Check out the XLS random-number generator.

1. Cooperative Phenomena in Chemical Reactions

Consider the auto-catalytic reaction (Lotka-Volterra reaction) $A \to P$, which can be decomposed into a number of intermediate steps:

$$A + x \xrightarrow{k_1} 2x \qquad \text{rate constant } k_1 = 2.4$$
$$x + y \xrightarrow{k_2} 2y \qquad \text{rate constant } k_2 = 4.2$$
$$y \xrightarrow{k_3} P \qquad \text{rate constant } k_3 = 5.1$$

which, in an actual reactor occur simultaneously. Here, the input reagent A is kept at a constant, but arbitrary concentration $A:=[A]$. Catalysts are provided with initial concentrations $x_0 = 1.5$, $y_0 = 1.0$. For ease of notation, quantities are given in "natural" units.

a) Write down the 3 corresponding rate equations for the associated elementary reactions defining the evolution $\{x(t), y(t)\}$. What is the role of the reagents x and y?

b) Determine the stationary concentrations X and Y for the intermediate products x and y as functions of the rate constants k_i and the concentration of the input reagent A.

c) Consider small variations of the system about the stationary concentrations by replacing in the rate equations $x(t) \rightarrow x(t) + \delta x(t)$ and $y(t) \rightarrow y(t) + \delta y(t)$. Noting the cancellations due to the solution in ***b***)), derive the differential rate equations for δx (*t*) and δy (*t*) to first order in the variations.

d) Explore solutions to the time dependent concentrations $\delta x(t)$ and $\delta y(t)$ of the form $\delta(t) = \delta(0) \cdot e^{i \cdot \varpi \cdot t}$ and their derivatives and show their periodic behavior.

e) Determine the dependence of the frequency ϖ of these oscillations on rate constants k_i and concentration of *A*.

2. Computer Sim: Coupled Chemical Reactions

$$
\begin{array}{lll}
A + x \xrightarrow{k_1} 2x & & rate\ k_1 = 2.4 \\
x + y \xrightarrow{k_2} 2y & & rate\ k_2 = 4.2 \\
y \xrightarrow{k_3} P & & rate\ k_3 = 5.1
\end{array}
$$

Modify a provided MS-Excel code to model the time evolution of this set of coupled reactions. Use the rate equations derived in task ***1*** above. Perform model calculations for different concentrations of the reagent (for example *A = 0.01, 0.05, 1.0,* etc.).

3. Construct and Track 1D Cellular Automata

Plotting the time evolution of the 1D CA #20 on a 10 x10 – (t, x) lattice grid produces a linear, staircase-like trail tending to the right-hand-side. For each of the tasks below, draw the code bar with the ordered set of bytes defining geometric survival conditions for the CA cel ***q***. In each case, start with the single occupied seed cell *q* at (t=0, x=5). Follow the prescribed time evolution by shading cells occupied in sequential time steps.

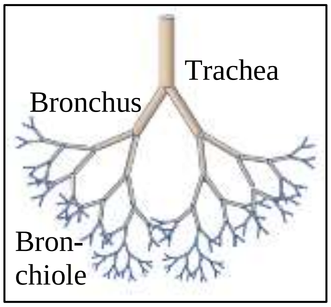
a) Design CA# LL that produces a mirror image of the CA#20 pattern, i.e. one tending to the left. Demonstrate the CA#LL pattern by marking the evolution for 4 time steps.

b) Design a new CA#LR by combining CA#20 with CA#LL in an inclusive logical OR of both sets of survival codes.

c) Shade the pattern for CA#LR for 8 time steps. Discuss the nature of evolved pattern (symmetry, repetition, density of area cover).

4. <u>Fractional Respiratory System</u>

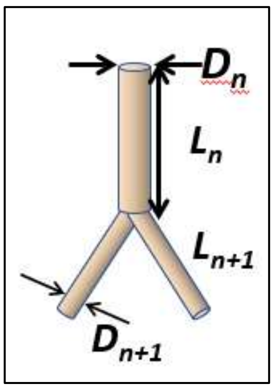
Consider the fractal model of the human respiratory system pictured in the drawing,



which exaggerates the actual L-R symmetry.

Doubling of the number of tubes and an associated reduction in diameter $\boldsymbol{D_n}$ and length $\boldsymbol{L_n}$ by a factor $\boldsymbol{R}$ repeats at each of $\boldsymbol{N} = 24$ levels.

For a typical human, $D_0 = 2$ cm, $D_{23} = 0.2$ mm.



From the data given above, calculate

a) the ratio D_n/D_0,

b) the scale factor R,

c) the total number of tubes,

d) the total length of all tubes, and

e) the total volume of all tubes.