

An integrated, quantitative introduction to the natural sciences

Problem Set 3

Due Monday, 8 October 2007

Problem 1: In the lecture notes we considered a simple algorithm for numerical solution of differential equations. The basic idea is to take

$$\frac{dc(t)}{dt} = -kc(t) \quad (1)$$

and replace it with

$$\frac{c(t + \Delta t) - c(t)}{\Delta t} = -kc(t) \Rightarrow c(t + \Delta t) = (1 - k\Delta t)c(t), \quad (2)$$

and then turn this rule directly into an algorithm.

- Consider the case where $k = 10 \text{ s}^{-1}$. Try various values for Δt (e.g., $\Delta t = 0.001, 0.01, 0.1, 1 \text{ s}$) and run your program for a number of iterations that corresponds to one second of real time. Compare your numerical results with the analytic solution $c_A(t) = c_A(0) \exp(-kt)$. How small does Δt need to be in order to get the right answer? How would your answer change if the rate k were ten times faster?
- Write the analogous program for a second order reaction, $A + B \xrightarrow{k_2} C$, described by the differential equations

$$\frac{dc_A}{dt} = -k_2 c_A c_B \quad (3)$$

$$\frac{dc_B}{dt} = -k_2 c_A c_B. \quad (4)$$

- Assume initial concentrations of $c_A(0) = 1 \text{ mM}$ and $c_B(0) = 2 \text{ mM}$. Let $k_2 = 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Before you run your program, what value of Δt seems reasonable? For how long (in real time) will you need to run in order to see most of the interesting dynamics?
- Run your program using the parameter settings from part [c]. Is there an analytic solution to which you can compare your results? If you don't have such a solution, how do you decide whether your program is giving the right answer?

Problem 2: Imagine that you do two experiments in chemical kinetics. In one case we watch the decay of concentration of some reactant A , and in the other case the reactant is B . The half lives of both species are about one minute, and perhaps because you are in a hurry you run the reactions out only for 2.5 minutes. You take samples of the concentration every quarter of a minute, and you get the results in Table 1. Perhaps the first thing you notice is that the concentrations don't decrease monotonically with time. Presumably this is the result of errors in the measurement.

- Can you decide whether the reactions leading to the decay of A and B are first order or second order? Are A and B decaying in the same way, or are they different?
- Other than making more accurate measurements, how could you extend these experiments to give you a better chance at deciding if the reactions are first or second order?

time t (minutes)	$[A]/[A]_0$	$[B]/[B]_0$
0.25	0.7157	0.7635
0.50	0.7189	0.4305
0.75	0.5562	0.5262
1.00	0.4761	0.6195
1.25	0.4948	0.4876
1.50	0.3096	0.3169
1.75	0.3842	0.3702
2.00	0.2022	0.2764
2.25	0.1872	0.2613
2.50	0.1971	0.2738

Table 1: Two kinetics experiments.

Problem 3: As discussed in connection with the first laboratory, an object moving through a fluid at relatively high velocities experiences a drag force proportional to the square of its velocity. In the presence gravity this means that $F = ma$ can be written as

$$m \frac{dv}{dt} = -av^2 + mg, \quad (5)$$

where the velocity v is positive if the object is moving downwards, a is the drag coefficient, and g as usual is the acceleration due to gravity. As noted in the lectures, a similar equations can arise in chemical kinetics.

- For any given system, the usual units of time, speed, etc. might not be very natural. Perhaps there is some natural time scale t_0 and a natural velocity scale v_0 such that if we measure things in these units our equation will look simpler. Specifically, consider variables $u \equiv v/v_0$ and $\tau \equiv t/t_0$. Show that by proper choice of t_0 and v_0 one can make all the parameters (m, g, a) disappear from the differential equation for $u(\tau)$.
- Solve the differential equation $u(\tau)$. Does this function have a universal shape? Since we have gotten rid of all the parameters, is there anything left on which the shape could depend? If you need help doing an integral it's OK to use a table (or perhaps an electronic equivalent), but you need to give references. Translate your results into predictions about $v(t)$.
- Suppose that the initial velocity $v(t = 0)$ is very close to the terminal velocity $v_\infty = \sqrt{mg/a}$. Show that your exact solution for $v(t)$ is approximately an exponential decay back to the terminal velocity. Then go back to Eq (5) and write $v(t) = v_\infty + \delta v(t)$, and make the approximation that δv is small, and hence δv^2 is even smaller and can be neglected. Can you now show that this approximate equation leads to an exponential decay of $\delta v(t)$, in agreement with your exact solution?