Case Study # 5: Two-Species Diffusion–Diurnal Kinetics
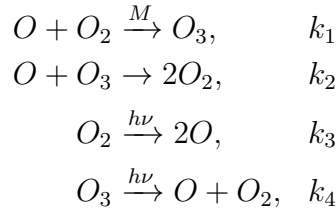
Background: Chang *et al.* [1, 2] have proposed approximate models to describe the chemical kinetics and transport phenomena associated with the dissociation of oxygen (O_2) into ozone (O_3) and monatomic oxygen (O) in the upper atmosphere. We are considering a one-dimensional version of such a model. The ambient oxygen concentration, c_3, is constant ($c_3 = 3.7 \times 10^{16}$). The concentrations of the two minor species, O and O_3, are $c_1(z,t)$ and $c_2(z,t)$, where z is the elevation above the earth's surface in km (here $30 \leq z \leq 50$) and t is time in seconds. Their transport is modeled using a reaction-diffusion equation,

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial z}\left[K(z)\frac{\partial c_i}{\partial z}\right] + R_i(\vec{c}, t)$$

The diffusive term is meant to represent the turbulent vertical transport with

$$K(z) = 10^{-8} \cdot \exp(z/5) \qquad [\text{km}^2/\text{s}]$$

The chemistry is described using the Chapman mechanism [2],

$$O + O_2 \xrightarrow{M} O_3, \qquad k_1$$
$$O + O_3 \rightarrow 2O_2, \qquad k_2$$
$$O_2 \xrightarrow{h\nu} 2O, \qquad k_3$$
$$O_3 \xrightarrow{h\nu} O + O_2, \quad k_4$$

The reaction rates, $R_i(\vec{c}, t)$, are given by

$$R_1(c_1, c_2, t) = -k_1 c_1 c_3 - k_2 c_1 c_2 + 2k_3(t)c_3 + k_4(t)c_2$$
$$R_2(c_1, c_2, t) = k_1 c_1 c_3 - k_2 c_1 c_2 - k_4(t)c_2$$

with,

$$k_1 = 1.63 \times 10^{-16}$$
$$k_2 = 4.66 \times 10^{-16}$$
$$k_\ell = \exp[-a_\ell/\sin\omega t] \text{ if } \sin\omega t > 0 \text{ and } 0 \text{ otherwise } (\ell = 3, 4)$$

with $a_3 = 22.62$, $a_4 = 7.601$, and $\omega = \pi/43200$ (43200 is a half a day measured in seconds).

This system is subject to the following initial and boundary conditions.

Initial Conditions

$$c_1(z, 0) = 10^6 \cdot \gamma(z)$$
$$c_2(z, 0) = 10^{12} \cdot \gamma(z)$$

with

$$\gamma(z) = 1 - \left(\frac{z-40}{10}\right)^2 + \frac{1}{2}\left(\frac{z-40}{10}\right)^4$$

Boundary Conditions — No flux at the top and bottom of the vertical atmospheric layer considered ($z = 30$ and $z = 50$).

Investigation:

- Implement a numerical solution of the system above discretized using the method of lines and central differencing for the diffusion term on a uniform mesh with M nodes as reported by Ref. [2].

- Use both a non-stiff solver (e.g. an explicit Runge-Kutta of order (4,5) such as `dropri5` in the `ode` module of `scipy` or `ode45` in Matlab) and a stiff solver (e.g. a method based on the backward differentiation formulas as implemented in the `bdf` method of `vode` in the `ode` module of `scipy` or `ode15s`, a variable order solver based on the numerical differentiation formulas in Matlab) and compare their performances (use a Table).

- Investigate the sensitivity of your results to mesh density.

- Compare your results to those published in [2]

NOTE: It is strongly recommended that you consult reference [2] to guide your solution.

Report: Prepare a report (3-4 pages max in ASME's two-colum article format, templates are available on-line) describing your work and including:

1. Short description of the problem

2. a description of your approach and a discussion of the results, including answers to the questions listed above.

3. Four Figures:

   - Plot to support your discussion of mesh sensitivity analysis.
   - Plot of c_1 and c_2 vs. time (from 0 to 10 days) at $z = 40$ km
   - Plot of c_1 vs. z at t=0, 2, 4, 6, 7, and 9 hours.
   - Plot of c_2 vs. z at t=0, 2, 4, 6, 7, 9, 12, 18, and 24 hours.

4. Conclusion.

The Report (single file, PDF format only) and your source code (`.py`, `.m`, `.f90`, `.cpp`, ... uploaded as a separate file together with non-standard libraries needed for compiling if relevant, please zip these files if there is more than one) are due on **December 14, 2014 at 5pm** and must be submitted electronically using the class SmartSite.

References

[1] J. S. Chang, Alan C. Hindmarsh, and N. K. Madsen. Simulation of chemical kinetics transport in the stratosphere. In R. A. Willoughby, editor, *Stiff Differential Systems*, p. 51. Plenum, New York, 1974.

[2] George D. Byrne and Alan C. Hindmarsh. *Journal of Computational Physics*, 70(1):1–62, 1987.