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Ordinary Differential Equations, Oscillating Chemical Reactions, and Chaos

Chaos has been found in many aspects of the phsyical world ranging from the weather to the human heartbeat [1]. Some concrete and definable examples of chaos can be seen in oscillating chemical reactions.

One example is the Belousov-Zhabotinskii reaction in chemistry, which was demonstrated in class. The basic reaction involves mixing two reactants at a constant flow rate; changing the flow rate can lead to periodic and even chaotic behavior.

The chemistry of the BZ reaction is rather complex, and involves the oxidation of easily brominated organic material by bromate ion in an acidic environment ([2],[3],[4]).

Slightly simpler is a similar reaction involving a three-variable autocatalator [5]. Autocalators involve isothermal reactions of chemicals in a thermodynamically closed environment – that is, reactions that maintain a constant temperature. Two-variable autocatalators have been successful in reproducing many types of chemical oscillations; a chemical modification by Peng et al. produced a three-variable autocalator which shows complex periodic as well as chaotic behavior. The chemistry of this reaction is as follows:

$$\begin{gathered} P \longrightarrow A \\ P + C \longrightarrow A + C \\ A \longrightarrow B \\ A + 2B \longrightarrow 3B \\ B \longrightarrow C \\ C \longrightarrow D \end{gathered}$$

This chemistry can be modeled by the following differential equations:

$$\begin{gathered} \frac{dA}{dt} = k_1 P + k_2 PC - k_3 A - k_4 AB^2 \\ \frac{dB}{dt} = k_3 A + k_4 AB^2 - k_5 B \\ \frac{dC}{dt} = k_4 B - k_5 C \end{gathered}$$

This can be converted into the following dimensionless form:

$$\begin{gathered} \frac{dX}{d\tau} = c_1 + c_2 Z - X - XY^2 \\ c_3 \frac{dY}{d\tau} = X + XY^2 - Y \\ c_4 \frac{dZ}{d\tau} = Y - Z \end{gathered}$$

In the equations above c_i are constants, and X, Y, and Z are proportional to A, B, and C respectively.

- Use Euler's method to find the solutions to the above set of equations using the constants c1=10, c2=0.15, c3=0.005 and c4=0.02. Plot log y versus time; does your graph oscillate? Use any plotting method that is convenient; GNUplot is a simple but powerful plotting tool (see help sheet on the course web page or man gnuplot).

- Now vary c2 from 0.10 to 0.18 using very small intervals (0.0005 or less). For each value of c2, plot the peaks on your oscillating graphs against the control variable (log y versus c2). This should give you a bifurcation diagram. Can you identify the regions of chaos on your diagram?

- There are a number of important variables which can alter your graph other than the control variable. Analyze how the number of iterations and time interval in Euler's method affect your graph. Also examine what happens if you start plotting peaks for the bifurcation diagram at the beginning of each oscillating graph versus after a number of iterations. Find an optimum algorithm and values, since the amount of computation involved will greatly increase in the next step.

- Instead of using Euler's method, use the fourth-order Runge-Kutta method for solution-finding. Adapt your algorithm to incorporate this. What differences do you find between Euler's method and Runge-Kutta? Do the graphs match up? If not, explain why.

- EXTRA CREDIT: In a famous paper entitled "Period Three Implies Chaos", mathematician James Yorke proved that in any one-dimensional system in which existed an oscillating state of three values there also existed chaos. Adapt your algorithm so that it finds the period of each oscillating graph. The period of a graph is the number of equilibrium peaks it has before repeating. Determine if and where a period of three is found. What does this imply about the system?

1 Further Reading

Chaos:
Euler's and Runge-Kutta Methods:

References

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