PATTERN FORMATION IN CHEMICAL REACTIONS

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Abstract

In this term paper, I will make a survey of pattern formation in chemical reactions. I will use the chlorine dioxide-iodine-malonic acid(CIMA1)[1] and chlorite-iodine-malonic acid(CIMA2)[10] reactions to explain two types of mechanism that lead to pattern formation. These are the Hopf bifurcation and the Turing instability respectively. This topic is important and interesting because it can shed light on the biological pattern formation problems.

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Contents

1 HISTORY

The study of pattern formation began in the early 1950s. Turing was the first note that pattern formation may occur in some chemical reactions as early as 1952[2]. These are reactions where diffusion is stronger than convection. The first experiment that validated Turing's proposal was the CIMA2 reaction in 1990[8]. Also in the early 1950s, a Russian biochemist called Boris Belusov observed oscillations in a mixed solution of citric acid and bromate ions in sulfuric acid with cerium catalyst. The oscillations were observed as color changes in the solution. This discovery was so radical at that time(1951)[4] that he could only publish this result in 1959 as an abstract in a medical proceeding[5]. Later, Zhabotinsky confirmed that this rection−It's called BZ reaction today−produces oscillations in densities of the chemicals with a period of a couple minutes.

2 HOPF BIFURCATION

Bifurcation is defined to be a qualitative change in the system's dynamics as a control parameter is varied. The value of the control parameter at the bifurcation is called the bifurcation point. A physical example is the buckling of a beam under a massive object. The weight of the object is the control parameter. If the weight is small the beam will retain its azimuthal symmetry. As we increase the weight, the beam will buckle at some critical weight.

To classify bifurcations, I will introduce a linearization method. Let's take a generic system of 2 dimensional nonlinear ordinary differential equations of the form:

$$\dot{x} = f(x, y), \;\; \dot{y} = g(x, y) \tag{1}$$

where f(x,y) and g(x,y) are arbitrary real functions of x and y. To linearize the system we will expand these functions around the fixed point(s) (x^*, y^*) of the system defined as:

$$f(x^*, y^*) = 0, \;\; g(x^*, y^*) = 0. \tag{2}$$

So at the fixed point(s) there is no change in the system. Expanding f(x,y) and g(x,y) in Taylor series to first order gives the following matrix equation:

$$\begin{pmatrix} \dot{x} \\ \dot{y} \end{pmatrix} = \frac{\partial(f,g)}{\partial(x,y)} \begin{pmatrix} x \\ y \end{pmatrix} \tag{3}$$

where we are measuring the x and y from the fixed point(s). The Jacobian is given by

$$\partial(f,g)/\partial(x,y) = \begin{pmatrix} \frac{\partial f}{\partial x} & \frac{\partial f}{\partial y} \\ \\ \frac{\partial g}{\partial x} & \frac{\partial g}{\partial y} \end{pmatrix}$$

(4)

and is evaluated at the fixed point(s). The behavior of the system around the fixed point(s) is determined by the eigenvalues and the eigenvectors of the Jacobian. An overall qualitative understanding can be achieved from this. Now, we can classify the fixed points. Let's define τ as the trace and λ as the determinate of the Jacobian. The eigenvalues are given by

$$\omega_{\pm} = \frac{1}{2}\left(\tau \pm \sqrt{\tau^2 - 4\lambda}\right) \tag{5}$$

If $\lambda < 0$, then the eigenvalues are real and have opposite signs. This means that the trajectories move towards the fixed point along one eigenvector and away from it along the other eigenvector. The linearized equations have solutions of the form $e^{\omega}t$. So positive ω means exponential growth away from the fixed point. Negative frequency gives approach to the fixed point.This kind of fixed point is a saddle point.

If $\lambda > 0$, then the eigenvalues are either real with the same sign(nodes), or they are complex conjugate(spirals or centers). The nodes with negative eigenvalues(repeller) repel all trajectories that are around them so they are unstable. The instability means that if the system is prepared in this state, it will move away from it. The nodes(attractors) with positive eigenvalues are stable and the system will be driven to it, if it sufficiently close to it. Spirals also have unstable and stable species. If the $\Re[\omega] > 0$, it's unstable -otherwise stable. Stable spirals spiral down to the fixed point. If the eigenvalues are pure imaginary, then we get a center which are periodic orbits. So the stability is determined by τ.

A limit cycle is an isolated periodic orbit. There are no closed orbits around it. If the neighboring trajectories approach to it, then it's stable. The limit cycle may also repel all trajectories from it(unstable). There are two other cases which are half-stable: trajectories approaching it from the inner part and moving away from it at the outside of it and vice versa. A stable limit cycle can be used to model self-sustained(not driven) oscillatory systems.

Now, we are ready to discuss Hopf bifurcations. This happens when a stable fixed point loses its stability as a parameter is varied. The stable fixed point has eigenvalues with positive real parts, and it can be a spiral with complex conjugate eigenvalues or an attractor. For our purposes, it's enough to consider

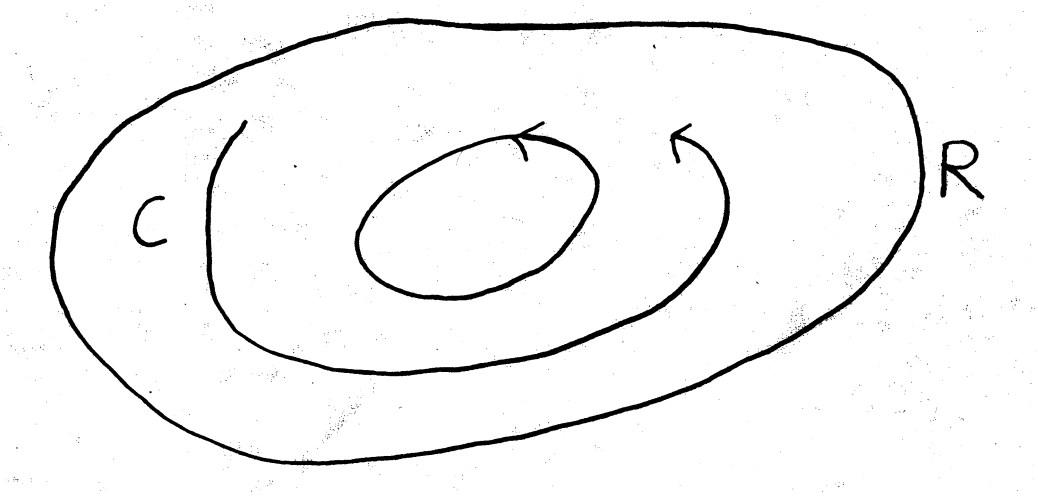

Figure 1: Poincaré-Bendixson theorem. (after[3])

the spirals. At the bifurcation point, the real part(it's the same for both eigenvalues) becomes 0. So, we have a center with a periodic orbit at this point. In a Hopf bifurcation, a limit cycle is created as a stable fixed point turns into an unstable one.

2.1 Poincaré-Bendixson Theorem

This is an existence theorem about limit cycles. The proof requires some knowledge of topology[7] and I will omit it. It applies to 2-dimensional systems.

Poincaré-Bendixson Theorem. Let R be a closed and bounded region in the plane which does not contain any fixed points. Now, we have an continuously differentiable vector field of the form eq. (1). If there is a trajectory C that stays inside R for all times, then C is a limit cycle(at least as $t \to \infty$). See figure 1.

This theorem is useful with a wise choice of region R which includes trajectories that stay inside it.

3 TURING INSTABILITY

Turing instability occurs in diffusive chemical reactions. Intuitively, it requires two key elements: an activator(x) whose concentration increases its own production and an inhibitor(y) which slows down the first reaction. If y diffuses more rapidly than x, then we might see Turing type pattern formation. These patterns are time independent and characterized by an universal wavelength. This wavelength does not depend on the geometry of the system, but it only

depends on the reaction parameters such as rates, concentrations and diffusion coefficients.
These systems can be modeled similar to Eq. 1[6]:

$$\frac{\partial x_i}{\partial t} = F_i(x,y) + D_i \Delta x_i,\ i = 1,2 \tag{6}$$

Here, x_i stands for x or y, F_i introduces the nonlinearity into the system, D_i are the relevant diffusion constants and Δ is the usual Laplacian. Other than F_i, this is the diffusion equation. We linearize the system by Taylor Series expanding:

$$\dot{x_i} = \left[\left(\frac{\partial(F_1, F_2)}{\partial(x,y)} \right)_{ij} - D_i k^2 \delta_{ij} \right] x_j, \tag{7}$$

where we have replaced Δ by $-k^2$ since we have taken a Fourier transform with respect to (x,y). If the Jacobian takes one of the following forms, the conditions listed in the beginning of the section are fulfilled:

$$(1)\ \begin{pmatrix} + & - \\ + & - \end{pmatrix} \quad (2)\ \begin{pmatrix} + & + \\ - & - \end{pmatrix} \tag{8}$$

The eigenvalues of the system are given by:

$$\omega_{\pm} = \frac{1}{2} \left(\Sigma \pm \sqrt{\Sigma^2 - 4\delta} \right), \tag{9}$$

where Σ is the trace and δ is the determinant of the matrix in Eq. 7. The instability occurs when one of the eigenvalues have a positive real part so the concentration goes like $e^{+\Re[\omega]t}$(to infinity). This will happen when the determinant of the Jacobian is positive and D_2 is sufficiently large.

4 THE CIMA1 REACTION

In this section, we study a simple model of the CIMA1 reaction, which shows oscillatory behavior. We will see that this is caused by a Hopf bifurcation. The experiment was performed in a continuous flow stirred tank reactor(CSTR). The densities were measured by a spectrometer. This complicated reaction can be represented by the following important steps whose speed has been determined by numerical calculations.

$$\mathrm{ClO_2} + I^- \rightarrow \{CIO_2I^-\} \quad (fast) \tag{10}$$
$$\{\mathrm{ClO_2}I^-\} \rightarrow CIO_2^- + I \quad (slow) \tag{11}$$
$$\mathrm{I{+}I} \rightarrow I_2 \quad (fast) \tag{12}$$

Numerical studies[10] have shown that the concentrations of ClO_2^-(Y) and I^-(X) change several order of magnitude while ClO_2, I_2 and MA does not vary much.

After non-dimensionalizing the rate equations become:

$$\dot{x} = a - x - \frac{4xy}{1+x^2}, \tag{13}$$

$$\dot{y} = bx\left(1 - \frac{y}{1+x^2}\right), \tag{14}$$

where x and y are the non dimensional rates of I^- and ClO_2^- respectively. Here, a and b are non-dimensional rate constants which are known through experiments. Fixed point is given by

$$x^* = \frac{a}{5},\ y^* = 1 + {x^*}^2 \tag{15}$$

This point is unstable for

$$b < b_c \equiv \frac{3a}{5} - \frac{25}{a}\ . \tag{16}$$

We know that the concentrations are bounded. Let's assume that the fixed point is unstable. So we can form a finite region R around this fixed point(but excluding the fixed point) which will trap the trajectories that begin it. See figure 2 So we know that this system has oscillatory solutions by the Poincaré-Bendixson theorem.

We also note that at as b decreases below b_c, the fixed point changes from a stable spiral to unstable spiral. The numerical solutions show that we have Hopf bifurcation. See figure 3

5 THE CIMA2 REACTION

To observe Turing instabilities, chemists designed the continuous flow un-stirred reactor(CFUR). See Figure 4. In CFUR, the reactions only occur in a thin layer of gel where the only relevant transport is via diffusion. The reaction is continuously fed with chemicals which diffuse into the reactor. In CIMA2, there is a difference in diffusion constants between I^-(activator) and ClO_2^-(inhibitor) because starch(a big molecule with low diffusion constant) couples to I^- and slows it down. Starch is also used to observe the pattern formation because it turns dark blue when there is a high I^- concentration. The reaction can be written as follows:

$$MA + I_2 \rightarrow IMA + I^- + H^+ \tag{17}$$

$$ClO_2 + I^- \rightarrow ClO_2^- + \frac{1}{2}I_2 \tag{18}$$

$$ClO_2^- + 4I^- + 4H^+ \rightarrow I^- + 2I_2 + 2H_2O \tag{19}$$

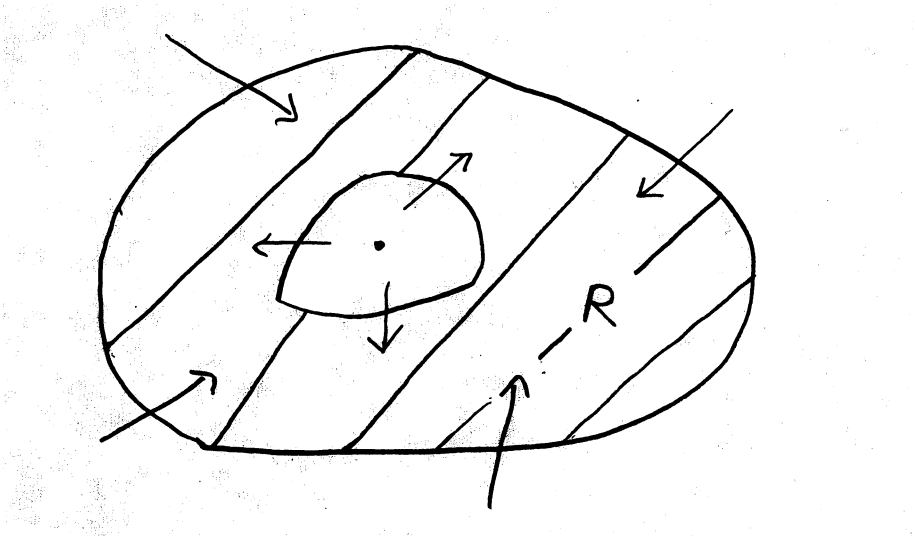

Figure 2: The shape of the region R. (after[3])

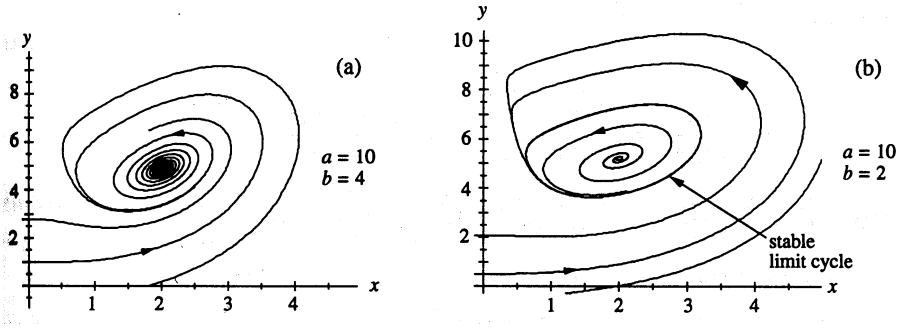

Figure 3: The numerical solutions to CIMA1 model shows a Hopf bifurcation. Here a=10, so $b_c = 3.5$. (after[3])

Numerical analysis shows that only the concentrations of I^- and ClO_2^- vary significantly. The rate equations are

$$\frac{\partial x}{\partial t} = r_1 - x - 4\frac{xy}{u+x^2} + \frac{\partial^2 x}{\partial z^2} \tag{20}$$

$$\frac{\partial y}{\partial t} = (1+K)\left[r_2\left(x - 4r_3\frac{xy}{u+x^2}+\right) + D\frac{\partial^2 x}{\partial z^2}\right] \tag{21}$$

Here the r_i are rate constants, and $D = D_2/D_1$. K is proportional to the starch concentration. x and y are the dimensionless concentrations of I^- and ClO_2^- respectively.The system will have a Turing instability if the following is true:

$$r_2 < D\ \frac{3r_1^2 - 125}{5r_1}\ \frac{4r_1 - \sqrt{10(r_1^2+25)}}{4r_1 + \sqrt{10(r_1^2+25)}}. \tag{22}$$

The universal wavelength is found to be 0.2 mm[8] by experiments. We can also have Hopf bifurcation for:

$$r_2 < \frac{1}{1+K}\ \frac{3r_1^2 - 125}{5r_1} \tag{23}$$

We can see that for $D \approx 1$ and K=0, Turing stability is screened and Hopf bifurcation occurs first as r_2 is decreased. However, the Hopf bifurcation moves to lower values of r_2 as K increases. Turing instability occurs first for

$$(1+K)D > \frac{4r_1 + \sqrt{10(r_1^2+25)}}{4r_1 - \sqrt{10(r_1^2+25)}} \tag{24}$$

The starch concentration doesn't effect the Turing instability, but drives the Hopf bifurcation away from it so that we can see Turing structures.

6 CONCLUSION

I have considered two mechanisms for pattern formation in chemical systems, and gave one experimental example for each them. It's remarkable that such complex systems can be described by 2-dimensional models. Actually, the CIMA2 system can have both type of behavior. Of course, the Hopf mechanism is stronger than the Turing instability because it produces time dependent patterns that will screen time independent patterns. There are types as well such as defect bifurcations, plastic bifurcations... One can see review articles for these[11,12]

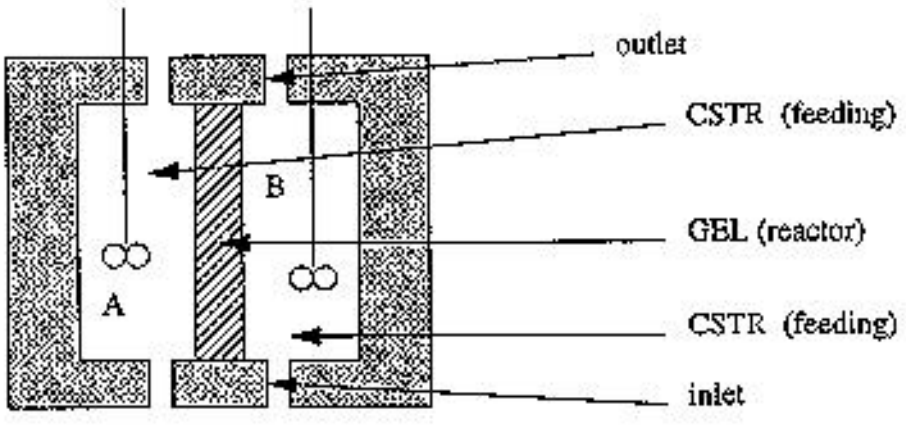

Figure 4: A typical continuous flow un-stirred reactor(CFUR) (after[9])

7 REFERENCES

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