Chaos and Complexity in Chemical Systems

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Chapter 1

Chaos and Complexity in Chemical Systems
1.1 Introduction

Complex chemical mechanisms are written as sequences of elementary steps satisfying detailed balance where the forward and reverse reaction rates are equal at equilibrium. The laws of mass action kinetics are applied to each reaction step to write the overall rate law for the reaction. The form of chemical kinetic rate laws constructed in this manner insures that the system will relax to a unique equilibrium state which can be characterized using the laws of thermodynamics.

Most chemically reacting systems that we encounter are not thermodynamically controlled since reactions are often carried out under non-equilibrium conditions where flows of matter or energy prevent the system from relaxing to equilibrium. Almost all biochemical reactions in living systems are of this type as are industrial processes carried out in open chemical reactors. In addition, the transient dynamics of closed systems may occur on long time scales and resemble the sustained behaviour of systems in non-equilibrium conditions. A reacting system may behave in unusual ways: there may be more than one stable steady state, the system may oscillate, sometimes with a complicated pattern of oscillations, or even show chaotic variations of chemical concentrations.

Analogous considerations apply to spatially distributed reacting media where diffusion is the only mechanism for mixing chemical species. Under equilibrium conditions any inhomogeneity in the system will be removed by diffusion and the system will relax to a state where chemical concentrations are uniform throughout the medium. However, under non-equilibrium conditions chemical patterns can form. These patterns may be regular, stationary variations of high and low chemical concentrations in space or may take the form of time-dependent structures where chemical concentrations vary in both space and time with complex or chaotic forms.

In this chapter we shall examine how such temporal and spatial structures arise in far-from-equilibrium chemical systems. We first examine spatially uniform systems and develop the theoretical tools needed to analyze the behaviour of systems driven far from chemical equilibrium. We focus especially on the nature of chemical chaos, its characterization and the mechanisms for its onset. We then turn to spatially distributed systems and describe how regular and chaotic chemical patterns can form as a result of the interplay between reaction and diffusion.

This account is not exhaustive but provides a guide to the main theoretical ideas and experimental methods that have emerged in this subject. Fuller accounts and broad background are given in recent books devoted to this topic. [1, 2, 3, 4, 5]
1.2 Chemical reactions as dynamical systems

Consider a spatially homogeneous reacting mixture where concentration gradients are removed by stirring or rapid diffusion of the chemical species. In this circumstance the instantaneous state of the system is described by a vector of chemical concentrations for the \( n \) chemical species, \( c(t) = (c_1(t), c_2(t), \ldots, c_n(t)) \), whose evolution is specified by the ordinary differential equations (ODEs) of mass action kinetics

\[
\frac{dc(t)}{dt} = R_M(c(t); k) .
\]

Here \( R_M(c(t); k) \) is a vector of reaction velocities which are usually nonlinear functions of the chemical concentrations whose form is determined by the reaction mechanism. The reaction velocities also depend on the chemical rate constants, collectively described by the vector \( k = (k_1, k_2, \ldots) \), for the steps in the reaction mechanism.

For a closed chemical system with a mass action rate law satisfying detailed balance these kinetic equations have a unique stable (thermodynamic) equilibrium, \( \lim_{t \to \infty} c(t) = c_{\text{eq}} \). In general, however, we shall be concerned with chemical reactions that are maintained far from chemical equilibrium by flows of reagents into and out of a continuously stirred tank reactor (CSTR). In this case the chemical kinetic equation (1.1) must be supplemented with flow terms

\[
\frac{dc(t)}{dt} = R_M(c(t); k) - k_f (c(t) - c_f) \equiv R(c(t); \mu) \quad (1.2)
\]

where \( k_f \) is the flow rate constant and \( c_f \) the vector of the feed concentrations. We have denoted the reaction rate in this general non-equilibrium case by \( R(c(t); \mu) \) with \( \mu \) as symbol for the collection of all parameters that characterize \( R \): rate constants, feed concentrations and flow rates. Suppose the flow terms increase from zero; then this open system’s stable state moves from the thermodynamic equilibrium, \( c_{\text{eq}} \), to a nearby, non-equilibrium steady state, \( c_s \), on the so-called thermodynamic branch. This non-equilibrium stable state of the system is the solution, \( c = c_s \), of \( R(c; \mu) = 0 \). However, if the flow terms become sufficiently large, this steady state becomes unstable and is replaced by new, non-equilibrium states characteristic of this well stirred system. (Transients mimicking the behaviour of the non-equilibrium states can be observed in closed reactors starting from initial conditions that are far from equilibrium.)

It is convenient to analyze these rate equations from a dynamical systems point of view similar to that used in classical mechanics where one follows the trajectories of particles in phase space. For the chemical rate law (1.2) the “phase space”, conventionally denoted by \( \Gamma \), is \( n \)-dimensional.
and the chemical concentrations, \(c_1, c_2, \ldots, c_n\), are taken as orthogonal coordinates of \(\Gamma\), rather than the particle positions and velocities used as the coordinates in mechanics. In analogy to classical mechanical systems, as the concentrations evolve in time they will trace out a trajectory in \(\Gamma\). Since the velocity functions in the system of ODEs (1.2) do not depend explicitly on time a given initial condition in \(\Gamma\) will always produce the same trajectory. The vector \(\mathbf{R}\) of velocity functions in (1.2) defines a phase-space (or trajectory) flow and in its often convenient to think of these ODEs as describing the motion of a fluid in \(\Gamma\) with velocity field \(\mathbf{R}(c; \mu)\).

### 1.2.1 Chemical attractors

Because of the underlying dissipative nature of the chemical systems that the ODEs (1.2) represent, they have another important property: any volume in \(\Gamma\) will shrink as it evolves. For a given set of initial chemical concentrations the time evolution under the chemical rate law will approach arbitrarily closely some final set of points in \(\Gamma\) after transients have decayed. This final set of phase-space points is the **attractor** and the set of all initial conditions that eventually reach the attractor is called its basin of attraction.

Attractors can be simple time-independent states (points in \(\Gamma\)), limit cycles (simple closed loops in \(\Gamma\)) corresponding to oscillatory variations of the chemical concentrations with a single amplitude, or chaotic states (complicated trajectories in \(\Gamma\)) corresponding to aperiodic variations of the chemical concentrations. To illustrate the representation of chemical dynamics in concentration phase space and the existence of chemical attractors, we consider the Willamowski-Rössler (WR) model chemical system based on the following reaction mechanism [6]

\[
A_1 + X_1 \underset{k_1}{\overset{k_1^*}{\rightleftharpoons}} 2X_1 \quad X_1 + X_2 \underset{k_2}{\overset{k_2^*}{\rightleftharpoons}} 2X_2 \quad A_5 + X_2 \underset{k_3}{\overset{k_3^*}{\rightleftharpoons}} A_2 \\
X_1 + X_3 \underset{k_4}{\overset{k_4^*}{\rightleftharpoons}} A_3 \quad A_4 + X_3 \underset{k_5}{\overset{k_5^*}{\rightleftharpoons}} 2X_3. \tag{1.3}
\]

The species \(A_1, A_2, \ldots, A_6\) are pool chemicals whose concentrations are assumed to be fixed by flows of reagents into and out of the reactor while \(X_1, X_2\) and \(X_3\) are the species whose concentrations vary with time. For mechanism (1.3) the mass action rate law is the system of ODEs

\[
\frac{dc_1}{dt} = k_1 c_{A_1}c_1 - k_{-1}c_1^2 - k_2 c_1 c_2 + k_{-2}c_2^2 - k_4 c_1 c_3 + k_{-4} \\
\frac{dc_2}{dt} = k_2 c_1 c_2 - k_{-2}c_2^2 - k_3 c_{A_2}c_2 + k_{-3}c_{A_2} \\
\frac{dc_3}{dt} = -k_4 c_1 c_3 + k_{-4} c_{A_3} + k_5 c_{A_3}c_3 - k_{-5}c_3^2. \tag{1.4}
\]
For this model the parameter set $\mu$ consists of the rate constants and the constant pool chemical concentrations $\{C_{AI}\}$. (Most chemical rate laws are constructed phenomenologically and often have cubic or other nonlinearities and irreversible steps. Such rate laws are reductions of the full underlying reaction mechanism.)

For certain parameter values this chemical system can exhibit fixed point, periodic or chaotic attractors in the three-dimensional concentration phase space. We consider the parameter set $\mu = \{k_1 c_{A_1} = 31.2, k_{-1} = 0.2, k_2 = 1.45, k_3 c_{A_2} = 10.8, k_{-3} c_{A_2} = 0.12, k_4 = 1.02, k_{-4} = 0.01, k_5 c_{A_4} = 16.5, k_{-5} = 0.5\}$. The rate constant $k_{-2}$ will be taken as the control or bifurcation parameter which is varied to examine how the system attractor changes. As an example, the single-banded chaotic attractor at $k_{-2} = 0.072$ for the WR model is shown in figure 1.1(a).

**Figure 1.1.** Panel (a) shows WR single-banded chaotic attractor for $k_{-2} = 0.072$. This attractor is projected onto the $(c_1, c_2)$ plane. The maximum value reached by $c_1(t)$ is $c_1^{\text{max}} \approx 54.1$ and the minimum reached by $c_1(t)$ is $c_1^{\text{min}} \approx 2.5$. The vertical line, at $c_1 = 8.5$ for $c_1 < 1$, shows the position of the Poincaré section of the attractor used later. Panel (b) shows a projection, onto the $(c_1(t_1), c_1(t_2))$ plane, of the chaotic attractor reconstructed from the set of delayed coordinates $\{c_1(t), c_1(t_1), c_1(t_2)\}$, where $t_1 = t + \tau_1$ and $t_2 = t + \tau_2$, for $0 \leq t < \infty$, and fixed delays $\tau_1 = 137$ and $\tau_2 = 200$. Note that both $c_1(t_1)$ and $c_1(t_2)$ reach a maximum of $c_1^{\text{max}}$ and a minimum of $c_1^{\text{min}}$ so that the three-dimensional reconstructed attractor is confined to a cube with sides of length $c_1^{\text{max}} - c_1^{\text{min}}$. The central hole of the attractor is bounded along the diagonal in a similar way.
1.2.2 Phase space reconstruction

The description of chemical reactions as trajectories in phase space requires that the concentrations of all chemical species be measured as a function of time, something that is rarely done in reaction kinetics studies. In addition, the underlying set of reaction intermediates is often unknown and the number of these may be very large. Usually, experimental data on the time variation of the concentration of a single chemical species or a small number of species is collected. (Some experiments focus on the simultaneous measurement of the concentrations of many chemical species and correlations in such data can be used to deduce the chemical mechanism. [7])

The trajectory description problem of chemical reactions is resolved by using phase-space reconstruction from a single time series [8]; this method uses delayed data at times: \( t, t+\tau_1, t+\tau_2, \ldots, t+\tau_{n-1} \) for an \( n \)-dimensional attractor, where usually \( n \leq 3 \). One may show that in place of the set of all chemical concentrations one may use, say, \( c_1 (t), c_1 (t + \tau_1), c_1 (t + \tau_2), \ldots \) to represent trajectories in the concentration phase space. Such phase-space reconstruction methods all rely on Whitney’s embedding theorem [9] which allows a multi-dimensional attractor to be reconstructed from a single time series. Since phase-space volumes contract for dissipative chemical systems, as noted above, the final attractor may have a dimension much smaller than the original \( n \)-dimensional phase space. The effective behaviour of the system may often be captured in a phase space of only few dimensions even though many chemical intermediates are involved. To illustrate this reconstruction method, the set of delayed \( c_1 \) coordinates for chaotic attractor shown in figure 1.1(a), viz. \( (c_1 (t), c_1 (t + \tau_1), c_1 (t + \tau_2)) \) for \( t \) going from zero to some large value, was used to reconstruct the topologically equivalent attractor shown in figure 1.1(b).
1.3 Chemical chaos

We shall now analyze the structure of a chemical strange attractor and describe why the dynamics may be classified as chaotic.

1.3.1 Strange attractors

We begin by describing the features of a strange attractor. Figure 1.1(a) was constructed from a single chaotic trajectory which corresponds closely to a chaotic strange attractor, meaning that any such chaotic trajectory would look similar. Any point in the basin of the attractor approaches it asymptotically. A point moving on the strange attractor at some time comes arbitrarily close to any other point lying in the attractor, so motion on the attractor is ergodic; this is necessary but not sufficient for chaotic behaviour. To be chaotic the motion on the attractor must be sensitive to initial conditions, so that as time increases points on the attractor, however close together they may be initially, separate to distances comparable to the size of the attractor over a sufficiently long time. The rate of separation is measured by the Lyapunov number. In order that such separation be compatible with bounded motion, i.e. with the observation that the strange attractor lies in a finite volume of phase space, the chaotic (phase-space) flow must stretch and folds back onto itself. If we imagine a parcel of (compressible) fluid in phase space we see that this folding implies creation of infinitely many layers like the repeated folding of mille-feuille pastry. Correspondingly, the chaotic attractor is the result of an infinity of similar foldings. This dynamical recursion produces a self-similarity or fractal structure in the chaotic attractor. In summary, the chaotic attractor displays (exponential) separation of points or orbit segments and self-similar structure in the way these orbit segments are arranged in space.

1.3.2 Poincaré sections and next-amplitude maps

For the strongly contracting phase volumes associated with chemical reactions, the three-dimensional continuous-time flow can be reduced to a one-dimensional discrete-time map as follows. We first construct the Poincaré section of the attractor flow. For the projection shown in figure 1.1(a) the flow is counter-clockwise implying \( c_1 < 0 \) above the central hole in the single-banded attractor. Therefore this flow will circulate round this hole and repeatedly intersect the Poincaré surface of section \( c_1 \equiv e_1 = 8.5 \), indicated by the heavy vertical line in panel (a), from right to left. Suppose that at time \( t_0 \) the trajectory intersects this Poincaré surface at a point \( (c_2(t_0), c_3(t_0)) \); at time \( t_1 \) it makes its next or so-called first return to the surface at point \( (c_2(t_1), c_3(t_1)) \). This process continues for times \( t_2, t_3, \ldots \), the difference \( t_{n+1} - t_n \) being the period of the \( n^{th} \) first-return trajectory segment. The sequence of points generated by these intersections is
the Poincaré section and is plotted in figure 1.2(a). The thin line-like form arises from the strong contraction of the flow onto the attractor; thus the attractor resembles a two-dimensional surface formed from extremely tightly compressed and folded layers; sufficiently close to the attractor the trajectories tend to separate from one another across the attractor band. The function that takes \((c_2(t_n), c_3(t_n))\) into \((c_2(t_{n+1}), c_3(t_{n+1}))\) is the Poincaré map. The line-like form of the Poincaré section and its single-valuedness

![Diagram](image)

**Figure 1.2.** Panel (a) shows the \((c_2, c_3)\) Poincaré surface of section of the phase flow, taken at \(c_1^\text{ext} = 8.5\) with \(c_1 < 0\), for the WR chaotic attractor at \(k_2 = 0.072\). Panel (b) shows the next-amplitude map constructed from pairs of intersection coordinates \(\ldots, (c_2(n + 1), c_3(n)), (c_2(n + 2), c_3(n + 1)), \ldots\). The sequence of horizontal and vertical line segments, each touching the diagonal \(B\) and the map, comprise a discrete trajectory. The direction on the first four segments is indicated.

as a function of either coordinate permits a one-dimensional representation of the two-dimensional Poincaré map. To do this second part of the next-amplitude map construction we plot the \(c_2\) component of the Poincaré map corresponding to the \(n\)th intersection of the chaotic trajectory with the Poincaré surface, \(c_2(n) \equiv c_2(t_n)\), versus its value at the \((n + 1)\)st intersection, \(c_2(n + 1) \equiv c_2(t_{n+1})\). This next-amplitude map is displayed in figure 1.2(b). The map has a quadratic extremum, a roughly parabolic shape, and is densely filled by intersection points. We may then represent trajectories of the flow by iterates of this map. To represent these iterates graphically, we first draw the bisectrix of the map, i.e. the diagonal line \(B\) in figure 1.2(b). By construction, any point on the map whose abscissa is \(c_2(n)\) has ordinate \(c_2(n + 1)\). This ordinate is given by moving horizontally to the bisectrix. Moving vertically from the bisectrix to the map makes
\( c_2(n+1) \) the new abscissa and \( c_2(n+2) \) the corresponding ordinate. These two steps correspond to an iteration of the next-amplitude map and the procedure can be repeated to obtain a discrete trajectory indicating how the chaotic attractor structure is built up. A portion of such a discrete chaotic trajectory is shown in figure 1.2(b).

### 1.3.3 Lyapunov number and fractal dimension

Chaotic attractors are complicated objects with intrinsically unpredictable dynamics. It is therefore useful to have some dynamical measure of the strength of the chaos associated with motion on the attractor and some geometrical measure of the structural complexity of the attractor. These two measures, the Lyapunov exponent or number [1] for the dynamics, and the fractal dimension [10] for the geometry, are related. To simplify the discussion we consider three-dimensional flows in phase space but the ideas can be generalized to higher dimension.

As already mentioned the motion of a chaotic flow is sensitive to initial conditions; [11] points which initially lie close together on the attractor follow paths that separate exponentially fast. This behaviour is shown in figure 1.3 for the WR chaotic attractor at \( k_{-2} = 0.072 \). The instantaneous rate of separation depends on the position on the attractor. However, a chaotic orbit visits any region of the attractor in a recurrent way so that an infinite time average of this exponential separation taken along any trajectory in the attractor is an invariant quantity that characterizes the attractor. If \( \gamma(t) \) is a trajectory for the rate law (1.2) then we can linearize the motion in the neighbourhood of \( \gamma \) to get

\[
\frac{d\delta c}{dt} = \frac{\partial R}{\partial c} \bigg|_\gamma \delta c.
\]  

(1.5)

The formal (or numerical) integration of this equation can be written as

\[
\delta c(t) = L(t)\delta c(0)
\]  

(1.6)

where \( L(t) \) is the displacement evolution matrix along \( \gamma \) and \( \delta c(t) \) is the solution of equation (1.5) for initial displacement \( \delta c(0) \). Then the Lyapunov number is defined by

\[
\lambda = \lim_{t \to \infty} \frac{1}{2t} \ln[\text{Tr} L(t)L(t)]
\]  

(1.7)

where \( L^\dagger \) is the adjoint of \( L \). If the Lyapunov number \( \lambda \) is positive this indicates chaotic behaviour since \( \lambda \) is a measure of (the exponent for) the average rate at which trajectories separate on the attractor.

A chaotic attractor comprises line-like trajectory segments and so is topologically a one-dimensional object. However, the trajectories may lie
Figure 1.3. The spreading of an ensemble of four points on the WR chaotic attractor is shown. Panel (a) shows the initial tight, four-point ensemble of open circles (○) at $c_2 = 5.287 \ldots$, $c_3 = 24.065 \ldots$ and variable $c_1 = 2.884 \ldots$, 2.984 \ldots, 3.084 \ldots, and 3.184 \ldots$ spreading to the set of four filled circles (●) at time $t = 4.0$ The filled circles overlap in two pairs. Panel (b) shows the spread from the same initial ensemble at time $t = 800.0$. The small dash in the centre of the initial ensemble (four ○'s) shows its narrow dispersion. The attractor is shown as a dust of stroboscopically plotted points so that the final ensemble of four filled circles (●) can be seen. One point lies on the inner edge of the central hole in the attractor. The density of the dust is an indicator of the coarse-grained density on the attractor.

arbitrarily close together in some regions of space, at least in the infinite time limit. In such regions a chaotic attractor has almost surface like “filling” properties. This unusual structure motivates the definition of a geometrical measure of chaos: the fractal, or more often, the box counting dimension of an attractor

$$D = \lim_{\epsilon \to 0} \frac{\ln N(\epsilon)}{\ln(1/\epsilon)} = -\lim_{\epsilon \to 0} \frac{\ln N(\epsilon)}{\ln \epsilon}. \quad (1.8)$$

where, in two-dimensional or three-dimensional space $N(\epsilon)$ is the minimum number of squares or cubes, respectively, of side $\epsilon$ that covers the attractor. This dimension can be calculated for the Poincaré section of the phase flow by covering it with successively smaller squares or for the entire attractor by covering it with successively smaller cubes and measuring $D$ as the slope of $N(\epsilon)$ versus $\ln(1/\epsilon)$ implied in (1.8). This dimension is typically non-integer and is less than the phase-space dimension.
1.3.4 Experimental observations of chemical chaos

The existence of chaotic oscillations has been documented in a variety of chemical systems. Some of the earliest observations of chemical chaos have been on biochemical systems like the peroxidase-oxidase reaction [12] and on the well known Belousov-Zhabotinskii (BZ) [13] reaction. The BZ reaction is the Cl ion catalyzed oxidation of citric or malonic acid by bromate ion. Early investigations of the BZ reaction used the techniques of dynamical systems theory outlined above to document the existence of chaos in this reaction. Apparent chaos in the BZ reaction was found by Hudson et al. [14] and the data were analyzed by Tomita and Tsuda [15] using a return-map method. Chaos was confirmed in the BZ reaction carried out in a CSTR by Roux et al. [16, 17] and by Hudson and Mankin [18] who also used reconstruction from the electrode potentials of Pt and Br, and d[Pt]/dt as independent variables. These demonstrations of true chemical chaos were achieved by a number of then new methods: power-spectral analysis, [16, 19] trajectory reconstruction in phase space, [16] and next-amplitude-map analysis. [15, 20, 21] The existence of true chemical chaos was signalled by a positive Lyapunov exponent calculated from the experimental return map. Since these early investigations chaos has been documented in a variety of chemical systems. One aspect of these CSTR experiments was the observation that the stirring rate moved the bifurcation point(s) even if this rate was very large. [22] This effect depends on turbulent mixing and can be controlled but not eliminated by keeping the stirring rate constant. We now give examples of two related dynamical systems techniques used by experimentalists: phase-space reconstruction of chaotic attractors, and the analysis of the associated next-amplitude maps. First we discuss a study where an attractor was reconstructed from experimental data and then used to obtain a next-amplitude map. [17]

Figure 1.4 (a) shows an experimental chaotic attractor reconstructed from the Br electrode potential, i.e. the logarithm of the Br ion concentration, in the BZ reaction [17]. Such reconstruction is defined, in principle, for continuous time t. However, in practice data are recorded as a discrete time series of measurements, \{X(t_i) : i = 1, 2, \ldots, T\}, consisting of thousands (\text{\textit{T}}) of data points. In our example \text{\textit{X}}(t_i) is proportional to \ln[Br^-](t_i). The experimental attractor was reconstructed [17] in the space of the three variables, \text{\textit{X}}(t_i), \text{\textit{X}}(t_i+\tau) and \text{\textit{X}}(t_i+2\tau), and panel (a) shows the projection of this attractor onto the (\text{\textit{X}}(t_i), \text{\textit{X}}(t_i+\tau)) plane. This attractor resembles that of the chaotic attractor shown in figure 1.1(a) and it can be demonstrated that the reconstructed attractor possesses the signatures of chaos; regions where trajectories locally spread or diverge and regions of re-injection and folding of the phase-space flow. Furthermore, we see that because the chaotic attractor is surface-like it has a fractal dimension close to two in spite of the fact that there are likely to be 30-40
chemical species involved in the reaction so that the Euclidean dimension of the full concentration phase space is large. This points to the usefulness of phase-space reconstruction methods for low-dimensional chaotic attractors, especially for systems with a high but unknown phase-space dimensionality.

We now examine how a next-amplitude-map was obtained from the attractor shown in figure 1.4 (a). [17] Consider the plane in this space whose projection is the dashed line in panel (a), i.e. a plane orthogonal to the \((X(t_i), X(t_i + \tau))\) plane. Then for the \(k^{\text{th}}\) intersection of the (continuous) trajectory with this plane there will be a data point \((X(t_{ik}), X(t_{ik} + \tau), X(t_{ik} + 2\tau))\) on the attractor that lies closest to the intersection of the continuous trajectory. A second discretization produces the set \(\{X_k \equiv X(t_{ik} + 2\tau) : k = 1, 2, \ldots, k_{\text{max}}\}\). This set is used in the construction of the next-amplitude map shown in panel (b) from the pairs of points \(\{(X_k, X_{k+1}) : k = 1, 2, \ldots, k_{\text{max}} - 1\}\). This map has a single quadratic extremum, similar to that of the WR model described in detail earlier. Such maps (together with the technical constraint of negative Schwarzian derivative) [23] possess \textit{universal} properties. In particular the universal (U) sequence in which the periodic orbits appear [24] was observed in the BZ reaction in accord with this picture of the chemical dynamics.
1.4 Routes to chaos

The next problem to consider is how chaotic attractors evolve from the steady state or oscillatory behaviour of chemical systems. There is, effectively, an infinite number of routes to chaos. [25] However, only some of these have been examined carefully. In the simplest models they depend on a single control or bifurcation parameter. In more complicated models or in experimental systems variations along a suitable curve in the control parameter space allow at least a partial observation of these well known routes. For chemical systems we describe: period doubling, mixed-mode oscillations, intermittency, and the quasi-periodic route to chaos.

1.4.1 Period doubling route to chaos

We first examine how chaos arises in the WR model using the rate constant $k_{-2}$ as the bifurcation parameter. However, another parameter or set of parameters could be used to explore the behaviour. (Independent variation of $p$ parameters produces a $p$-dimensional bifurcation diagram.) In the context of experiments carried out in CSTRs the bifurcation parameter is usually taken to be the flow rate or a reservoir concentration. If we start with a value of $k_{-2} > 0.1715$ with all other rate constants fixed at the values given in section 1.2, the WR reaction has a stable steady state or fixed point. We examine the sequence of transformations that takes place as $k_{-2}$ decreases. At a certain value of $k_{-2} = k_{-2}^H \approx 0.1715$ the fixed point, $(c_1^H, c_2^H, c_3^H) \approx (8, 8, 11.494, 15.048)$, loses its stability and the concentrations begin to oscillate with period $T_0$. This is the Hopf bifurcation point and for $k_{-2} < k_{-2}^H$ the chemical attractor is a limit cycle. As $k_{-2}$ decreases further the amplitude of the limit cycle grows (initially as $|k_{-2} - k_{-2}^H|^{1/2}$ until the system undergoes a further bifurcation at $k_{-2} \approx 0.1 \ldots$ where the orbit undergoes a subharmonic bifurcation and its period doubles. To understand this bifurcation imagine that the limit cycle lies on the surface of a Möbius band which is effectively a strip with a single twist in it. Motion on this band represents the slow relaxation of the system. At bifurcation the limit cycle becomes unstable but a stable orbit is born adjacent to it in the strip; this newborn orbit is geometrically equivalent to the edge of the Möbius strip as the width of the strip becomes arbitrarily small; because of the twist, the strip has only one edge of twice the length of the unstable limit cycle it contains. Therefore the new stable orbit has twice the period of its parent limit cycle. An infinite sequence of these local twists or braids occurs in the phase flow generating an infinite subharmonic sequence of period-doubled orbits. The first two orbits of the main WR sequence are shown in figure 1.5; there is a period-4 attractor at $k_{-2} = 0.095$. The $n^{th}$ period doubling the period of the oscillation is $T_n \approx 2^n T_0$. In the limit $n \to \infty$ we arrive at the strange attractor where
the time variation of the concentrations is no longer periodic. This is the *period-doubling route* to chaos.

![Figure 1.5](image)

**Figure 1.5.** The first two periodic orbits in the main subharmonic sequence are shown projected onto the $(c_1, c_2)$ plane. This sequence arises from Hopf bifurcation of the stable fixed point for the parameters given in the text. The arrows indicate the direction of motion. Panel (a) shows the limit cycle or period-1 orbit at $k_{-2} = 0.11$. Panel (b) shows the first subharmonic or period-2 orbit at $k_{-2} = 0.095$.

It is instructive to view this sequence of transformations in terms of a bifurcation diagram. We use the procedure described earlier to examine the chaotic orbit: the intersections of the periodic trajectories with the Poincaré surface are recorded for each value of the rate constant $k_{-2}$. In figure 1.6 we plot the concentration $c_2$ on the Poincaré plane versus $k_{-2}$. One can clearly see the sequence of period-doubling bifurcations leading eventually to the chaotic attractor. One can understand the origin of this sequence of bifurcations by considering the the next-amplitude map discussed earlier. We remarked in section 1.3.2 that this map has the nearly parabolic functional form shown in figure 1.2(b) so that, after suitable scaling, we can write the next-amplitude map in the standard quadratic form $c_2(n+1) = \lambda c_2(n)(1 - c_2(n))$, thereby preserving the local and global features of the bifurcation diagram 1.6. We know what happens as the standard map parameter $\lambda$ is changed. This reduction of the problem to the study of a quadratic map allows one to make a detailed examination of the universal properties of this route to chaos since the only requirement is that the map function be quadratic in the vicinity of its maximum. Such an analysis was carried out by Feigenbaum [26] where the following scaling relation was derived: let $\lambda_n$ be the value of $\lambda$ at the $n^{th}$ period doubling
Figure 1.6. The figure shows the $c_2$ coordinate, for $c_1 < 0$, of the family of trajectories intersecting the $(c_2, c_3)$ Poincaré surface at $c_1 = 8.5$ as a function of bifurcation parameter $k_{-2}$. As the ordinate $k_{-2}$ decreases the first subharmonic cascade is visible between $k_{-2} \approx 0.1$, the value of the first subharmonic bifurcation to $k_{-2} \approx 0.083$, the subharmonic limit of the first cascade. Periodic orbits that arise by the tangent bifurcation mechanism associated with type-I intermittency (see text for references) can also be seen for values of $k_{-2}$ smaller than this subharmonic limit. The left side of the figure ends at $k_{-2} = 0.072$, the value corresponding to the chaotic attractor shown in figure 1.1(a). Other regions of chaos can also be seen.

and $\lambda_c$ be its value in the $n \to \infty$ limit. Then for sufficiently large $n$, $\lambda_n - \lambda_c = \delta(\lambda_{n+1} - \lambda_c)$ with $\delta = 4.6692 \ldots$ a universal number for such period-doubling cascades for quadratic maps.

1.4.2 Other routes to chaos

In addition to the period-doubling route to chaos there are other routes that are chemically important: mixed-mode oscillations, intermittency, and quasi-periodicity. Their signature is easily recognized in chemical experiments, so that they were seen early in the history of chemical chaos.

Mixed mode oscillations (MMOs) have been observed in many experiments. Typically, an MMO consists of one or more large amplitude oscillations followed by several small amplitude oscillations. The size of the small oscillations may grow slowly. Suppose $L$ large oscillations are followed by $s$ small oscillations, where $L$ and $s$ are integers, then this MMO can be encoded by $L^s$. For example one large oscillation followed by one small oscillation is written $1^1$, and so on. Since large and small have a spe-
specific meaning in a series of chemical experiments we may find only small oscillations, encoded 0\textsuperscript{1} or only large oscillations encoded 1\textsuperscript{0} in the series. Chaotic MMOs consist of $L^*$ oscillations interspersed randomly by $L^*$, $L^{**}$, or $L^{***}$ oscillations. Experimental observations and theoretical descriptions for the origins of such oscillations have been given. [27]

Intermittency, in the context of chaotic dynamical systems, is characterized by long periods of nearly periodic or “laminar” motion interspersed by chaotic bursts of random duration. [28] Within this broad phenomenological description three kinds of intermittency have been distinguished theoretically and some detected experimentally. [1, 29] The onset of the laminar phase is statistical but its subsequent evolution is deterministic until the start of the next burst, whereas the behaviour of the chaotic phase is largely probabilistic. For this kind of onset of chaotic motion the bifurcation parameter, $\varepsilon$ say, is close to its critical bifurcation value $\varepsilon_c$ for periodic motion. As $\varepsilon$ passes from a “chaotic” value through $\varepsilon_c$ the motion goes from intermittent to marginally stable, to strictly stable periodic motion.

The quasiperiodic route to chaos is historically important. It arises from a succession of Hopf bifurcations. As already noted, a single Hopf bifurcation results in a limit cycle. The next Hopf bifurcation produces a phase flow that can be represented on the surface of a torus (doughnut). This flow is associated with two frequencies; if the ratio of these frequencies is irrational then the torus surface is densely covered by the phase trajectory, whereas if the ratio is rational the orbit winds periodically on the torus surface with both frequencies determining the overall period. However, a further Hopf bifurcation leads to an unstable torus flow which deforms into a chaotic flow. The nature of this instability was first discussed independently by Kupka and Smale; an equivalent theory of this breakdown of quasi-periodic flow to chaotic flow was proposed by Ruelle and Takens and was developed by them and Newhouse. [30] The quasiperiodic route to chaos was important because it was the first example of a transition to chaos that involved few modes, in contrast to the classical model of Landau of a gradual wandering into chaos as successive modes became unstable.
1.5 Chemical patterns and spatio-temporal chaos

Thus far we have considered systems where stirring ensured homogeneity within the medium. If molecular diffusion is the only mechanism for mixing the chemical species then one must adopt a local description where time-dependent concentrations, $c(r, t)$, are defined at each point $r$ in space and the evolution of these local concentrations is given by a reaction-diffusion equation

$$\frac{\partial c(r, t)}{\partial t} = R(c(r, t); \mu) + D \nabla^2 c(r, t)$$

(19)

where $D$ is a matrix of diffusion coefficients. In addition to the temporal behaviour described above, one now has the possibility of chemical pattern formation which may lead to spatio-temporal chaos. In order to investigate chemical pattern formation under controlled non-equilibrium conditions, experiments are now carried out in continuously fed unstirred reactors (CFUR). [31] In such reactors well stirred reagent baths are in contact with a gel or porous medium within which the chemicals mix and react in the absence of stirring effects other than diffusion. Since the reagent baths are CSTRs they continuously supply and remove reactants and products from the reaction-diffusion medium and chemical pattern formation can be controlled and maintained indefinitely. This has allowed experimentalists to make detailed studies of chemical pattern formation.

We shall describe some of the common types of chemical patterns observed in such experiments and comment on the mechanisms for their appearance. In keeping with the theme of this chapter we focus on states of spatio-temporal chaos or on regular chemical patterns that lead to such turbulent states. We shall touch only upon the main aspects of this topic since there is a large variety of chemical patterns and many mechanisms for their onset. [2, 3, 5, 32]

1.5.1 Excitable media

Excitable media are some of the most commonly observed reaction-diffusion systems in nature. An excitable system possesses a stable fixed point which responds to perturbations in a characteristic way; small perturbations return quickly to the fixed point, while larger perturbations that exceed a certain threshold value make a long excursion in concentration phase space before the system returns to the stable state. In many physical systems this behaviour is captured by the dynamics of two concentration fields, a fast activator variable $u$ with cubic nullcline and a slow inhibitor variable $v$ with linear nullcline. [33] The FitzHugh-Nagumo equation [34], derived as a simple model for nerve impulse propagation but which can also apply to a chemical reaction scheme [35], is one of the best known equations with
such activator-inhibitor kinetics

\[
\begin{align*}
\frac{du}{dt} &= -u^3 + u - v = R_u(u,v) \\
\frac{dv}{dt} &= \varepsilon(v - au + b) = R_v(u,v).
\end{align*}
\] (1.10)

Figure 1.7(a) shows the \( \dot{u} = 0 \) and \( \dot{v} = 0 \) nullclines of this system along with trajectories corresponding to sub- and super-threshold excitations. The

![Figure 1.7](image)

**Figure 1.7.** Cubic \( (u = 0) \) and linear \( (\dot{v} = 0) \) nullclines for the FitzHugh-Nagumo equation: panel (a) displays the excitable domain showing trajectories resulting from sub- and super-threshold excitations; panel (b) displays oscillatory domain showing limit cycle orbits; small inner limit cycle close to Hopf point; large outer limit cycle far from Hopf point.

trajectory arising from the sub-threshold perturbation quickly relaxes back to the stable fixed point. Three stages can be identified in the trajectory resulting from the super-threshold perturbation: an excited stage where the phase point quickly evolves far from the fixed point, a refractory stage where the system relaxes back to the stable state and is not susceptible to additional perturbation and the resting state where the system again resides at the stable fixed point.

An excitable medium is a diffusively coupled array of such local excitable elements described by the reaction-diffusion equation (1.9) with \( \mathbf{R} \) given by (1.10) and \( \mathbf{c} = (u,v) \). Imagine a local super-threshold perturbation applied to the system in the homogeneous resting state. Due to diffusive coupling, the perturbation will excite neighbouring regions of the medium. The originally perturbed region will then relax to the refractory stage where it is no longer susceptible to perturbation, and finally back to the stable steady state. Consequently, a circular wave of excitation with a
refractory tail will propagate outward through the medium (cf. figure 1.8, left panel). If the excitable system is periodically stimulated in a local region of the medium (a pacemaker region) a target pattern comprising a set of concentric rings of excitation will be observed.

If an excitable wave is broken, for instance, by an obstacle or inhomogeneity in the medium, since the front velocity is smaller at the tip than the rest of the wave front, free ends of wave fronts will curl leading to the formation of spiral waves in the system. An example of a spiral wave is shown in figure 1.8, right panel.

![Figure 1.8. Left panel shows a growing ring of excitation in an excitable FitzHugh-Nagumo medium; right panel shows a spiral wave in the same system.](image)

Excitable waves are seen in many chemical and biological systems. The often studied BZ reaction was one of the first systems in which such waves were observed [13, 36]. Chemical waves of this type have been studied extensively in catalytic oxidation of CO on Pt. [37] In biological contexts waves of this type occur in the aggregation stage of the slime mould dictyostelium discoideum where the chemical signalling is through periodic waves of cAMP; also the Ca$^{2+}$ waves in systems like xenopus laevis oocytes and pancreatic $\beta$ cells fall into this category. [38] Electrochemical waves in cardiac and nerve tissue have this origin and the appearance and/or breakup of spiral wave patterns in excitable media are believed to be responsible for various types of arrhythmias in the heart. [39, 40] Figure 1.9 shows an excitable spiral wave in dog epicardial muscle. [41]

The cores of the spiral waves need not be stationary and can move in periodic, quasi-periodic or even chaotic “flower” trajectories. [42, 43] In addition, spatio-temporal chaos can arise if such spiral waves break up and the spiral wave fragments spawn pairs of new spirals. [42, 44]
1.5.2 Oscillatory and chaotic media

We described earlier how a stable steady state may give rise to a periodic oscillation through a Hopf bifurcation. The steady state of the FitzHugh-Nagumo model can undergo such a Hopf bifurcation. Consider the situation shown in figure 1.7(b) for \( b = 0 \) where there is a single fixed point at the origin \((u^*, v^*) = (0, 0)\). This fixed point is stable if \( \varepsilon > a^{-1} \), \( a < 1 \), and becomes unstable at \( \varepsilon = \varepsilon_H = a^{-1} \) through a Hopf bifurcation spawning a limit cycle encircling the origin.

Consider the analog of such a bifurcation in a spatially distributed system and imagine tuning a bifurcation parameter \( \mu \) (in the parameter set \( \mu \)) in (1.9) through such a bifurcation point, \( \mu_H \) and let \( \lambda = |\mu - \mu_H|^{1/2} \) gauge the distance from the bifurcation point. One may then expand the local concentration about the steady state \( c^* \) as \( c(r, t) = c^* + A(r, t)\hat{e} + \text{c.c.} \), where \( A(r, t) \) is a complex amplitude and \( \hat{e} \) is an eigenvector of the linearized reaction-diffusion problem. Then, in the vicinity of the Hopf bifurcation point, it is possible to transform the reaction-diffusion equation into a universal equation for the complex amplitude \( A(r, t) \) [45]

\[
\frac{\partial A(r, t)}{\partial t} = A - (1 + i\beta)|A|^2 A + (1 + i\alpha) \nabla^2 A . \tag{1.11}
\]

This complex Ginzburg-Landau equation describes the space and time variations of the amplitude \( A \) on long distance and time scales determined by the parameter distance from the Hopf bifurcation point. The parameters \( \alpha \) and \( \beta \) can be determined from a knowledge of the parameter set \( \mu \) and the diffusion coefficients of the reaction-diffusion equation. For example, for the FitzHugh-Nagumo equation we have \( \alpha = (D_v - D_u)/[\omega_0(D_v + D_u)] \) and \( \beta = -1/\omega_0 \). The Ginzburg-Landau equation parameters may also be
extracted from the experimental data and this has been done for the BZ reaction. [46] Through such an analysis one can study general features of oscillatory media, independent of specific features of the reaction kinetics.

The complex Ginzburg-Landau equation also supports spiral wave solutions. [47] The core of a spiral wave is a point topological defect where the complex amplitude $A$ vanishes. [48] In certain parameter regions, one finds a type of spatio-temporal chaos termed defect-mediated turbulence where the average number of topological defects is stationary but their instantaneous number fluctuates: defects of opposite topological charge may collide and annihilate or defects may nucleate in pairs as a result of “pinching” of wave fronts. [49] Figure 1.10 shows the system in the defect-mediated turbulence regime and illustrates distribution of spiral defects in the turbulent dynamics described above. Such defect-mediated turbulence has been ob-

**Figure 1.10.** Defect-mediated turbulence in the complex Ginzburg-Landau equation. The left panel shows the phase, $\text{arg}(A)$, as grey shades while the right panel shows the amplitude, $|A|$, with a similar color coding. In the left panel topological defects can be identified as points around which one finds all shades of grey. Note the apparently random spatial pattern of amplitudes.

served in experiments on the BZ reaction. [50] The left panel of figure 1.11 shows the chemical pattern near the onset of the instability giving rise to spatio-temporal turbulence. Note that small well defined spirals can still be seen embedded in a sea of turbulent dynamics while in the right panel well beyond the instability one sees fully developed turbulence.

The local dynamics of the systems considered thus far has been either steady or oscillatory. However, we may consider reaction-diffusion media where the local reaction rates give rise to chaotic temporal behaviour of the sort discussed earlier. Diffusional coupling of such local chaotic elements can lead to new types of spatio-temporal periodic and chaotic states. It is possible to find phase-synchronized states in such systems where the am-
amplitude varies chaotically from site to site in the medium but a suitably defined phase is synchronized throughout the medium. [51] Such phase synchronization may play a role in layered neural networks and perceptive processes in mammals. Somewhat surprisingly, even when the local dynamics is chaotic, the system may support spiral waves. [52, 53, 54] The origin of such spiral waves in chaotic media can again be traced to the phenomenon of phase synchronization. The notion of a defect at the core of the spiral remains valid even for these chaotic media so the phase-coherent dynamics necessary for the existence of a spiral wave survives the amplitude turbulence. New phenomena can arise: in addition to point topological defects one can find synchronization line defects whose dynamics may be chaotic. Such synchronization line-defect dynamics has been observed in the BZ medium reaction. [54, 55, 56]

1.5.3 Turing patterns

If the diffusion coefficients of the chemical species are sufficiently different new types of chemical instability arise which can lead to the formation of chemical patterns and ultimately to spatio-temporal chaotic behaviour.

One of the best known such instabilities is the Turing bifurcation proposed in 1952 as a possible mechanism for morphogenesis. [57] While the relevance of this type of pattern-forming instability for biological systems is still a matter of debate, such Turing patterns have been observed in laboratory chemical experiments. [58, 59, 60] A Turing bifurcation involves the destabilization of a homogeneous steady state to form an inhomoge-
neous state or chemical pattern whose wavelength depends on the kinetic
parameters and diffusion coefficients of the system. Turing bifurcations
are often discussed in terms of activator-inhibitor kinetics like that of the
FitzHugh-Nagumo equation above. [61] Consider two chemical species, \( X_1 \)
and \( X_2 \), with concentration vector, \( \mathbf{c} = (c_1, c_2) \), that satisfies a two-variable
reaction-diffusion equation where, as usual \( \mathbf{R}(\mathbf{c}) \) describes the kinetics and
\( \mathbf{D} \) is a diagonal diffusion-coefficient matrix with elements \( D_1 \) and \( D_2 \). We
suppose the system possesses a homogeneous stable state, \( \mathbf{c}^* \), ob-
tained from the solution of \( \mathbf{R}(\mathbf{c}^*) = 0 \). To determine the conditions for a
Turing bifurcation to occur we consider the perturbation of this homoge-
neous steady state to \textit{inhomogeneous} perturbations, \( \mathbf{c}(\mathbf{r}, t) = \mathbf{c}^* + \delta \mathbf{c}(\mathbf{r}, t) \).
We may linearize the reaction-diffusion to obtain
\[
\frac{\partial \delta \mathbf{c}(\mathbf{r}, t)}{\partial t} = \mathbf{A} \delta \mathbf{c}(\mathbf{r}, t) + \mathbf{D} \nabla^2 \delta \mathbf{c}(\mathbf{r}, t)
\]  
(1.12)
where \( \mathbf{A} = (\partial \mathbf{R}/\partial \mathbf{c})_{\mathbf{c}=\mathbf{c}^*} \) is the matrix that specifies the chemical rate
evolution about the steady state \( \mathbf{c}^* \). To determine the stability of the
steady state it is useful to examine the behaviour of the Fourier compo-
nents of the concentration field, \( \hat{\mathbf{c}}_k \) which satisfy the Fourier transform of equation (1.12)
\[
\frac{\partial \hat{\mathbf{c}}_k(t)}{\partial t} = (\mathbf{A} - k^2 \mathbf{D}) \hat{\mathbf{c}}_k(t) \equiv \mathbf{B} \hat{\mathbf{c}}_k(t) .
\]  
(1.13)
Now we may state the well known conditions for a Turing bifurcation. If
\( A_{11} > 0 \) and \( A_{22} < 0 \) we say species \( X_1 \) is the activator and species \( X_2 \)
is the inhibitor. Then for a Turing bifurcation to occur we must have
det \( \mathbf{B} = 0 \), Tr \( \mathbf{B} > 0 \) and \( A_{11} D_2 + A_{22} D_1 > 0 \). The (unique) wavenumber
at the bifurcation is
\[
k_c = \left( \frac{\det \mathbf{A}}{D_1 D_2} \right)^{\frac{1}{4}}.
\]  
(1.14)
Furthermore, since the bifurcation must occur from a stable homogeneous
steady state we must have \( D_1 / D_2 < 1 \); i.e. the diffusion coefficient of the
inhibitor is greater than that of the activator. The critical diffusion ratio
at the bifurcation is
\[
\frac{D_1}{D_2} = A_{22}^{-1} \left( \det \mathbf{A} - A_{12} A_{21} + 2(A_{12} A_{21} \det \mathbf{A})^{1/2} \right) .
\]  
(1.15)
Consequently, when \( D_1 / D_2 \) exceeds the critical value, close to the bifur-
cation one expects to see the appearance of chemical patterns with char-
acteristic length \( \ell = 2\pi/k_c \). Beyond the bifurcation point a band of wave
numbers is unstable and nature of the pattern selected (spots, stripes,
etc.) depends on the nonlinearity and requires a more detailed analysis.
Chemical Turing patterns were observed in the chlorite-iodide-malonic acid
(CIMA) system in a gel reactor. [58, 59, 60] Figure 1.12, left panel, shows an experimental CIMA Turing spot pattern. [59]

The Turing mechanism requires that the diffusion coefficients of the activator and inhibitor be sufficiently different; but the diffusion coefficients of small molecules in solution differ very little. The chemical Turing patterns seen in the CIMA reaction used starch as an indicator for iodine. The starch indicator complexes with iodide which is the activator species in the reaction. As a result the complexing reaction with the immobilized starch molecules must be accounted for in the mechanism and leads to the possibility of Turing pattern formation even if the diffusion coefficients of the activator and inhibitor species are the same. [62]

One may also observe a transition to a type of defect-mediated turbulence in this Turing system (cf. figure 1.12, right panel). Here the defects divide the system into domains of spots and stripes. The defects move erratically and lead to a turbulent state characterized by exponential decay of correlations. [59] Turing bifurcations can interact with the Hopf bifurcations discussed above to give rise to very complicated spatio-temporal patterns. [63, 64]

1.5.4 Chemical front instabilities

Another class of instabilities that are driven by differences in the diffusion coefficients of the chemical species determines the shapes of propagating chemical wave and flame fronts. [65, 66]

As an example of chemical front instability consider a simple cubic autocatalytic reaction, \( A + 2B \rightarrow 3B \), occurring in a two-dimensional geometry where the “fuel” \( A \) occupies the right-hand region and the autocatalyst
occupies the left-hand region. [67] We suppose the reaction occurs under isothermal conditions which can be achieved for condensed phase reactions. The species $B$ will consume the fuel $A$ and the chemical front that separates the $A$ and $B$ species will move to the right. (For flame fronts one must generally couple the reaction kinetics to the variations in the temperature of the system.)

If the diffusion coefficient of species $A$ is less than that of $B$ ($D_A < D_B$) the propagating front will be planar. However, if $D_A$ is sufficiently greater than $D_B$, the planar front will become unstable to transverse perturbations and chaotic front motion will ensue. To understand the origin of the mechanism of the planar front destabilization consider the following: suppose the interface is slightly non-planar. We would like to know if the dynamics will tend to eliminate this non-planarity or accentuate it. Let $D_B \gg D_A$. The situation is depicted schematically in figure 1.13 where large diffusion fluxes are indicated by \( \rightarrow \) and smaller diffusion fluxes by \( \rightarrow \). For the part of the $B$ front that protrudes into the $A$ region, fast diffusion

\[ D_A < D_B \]

\[ D_A > D_B \]

**Figure 1.13.** Schematic picture of how the front instability arises for the case (a) $D_B \gg D_A$ and (b) $D_B \ll D_A$.

of $B$ leads to dispersal of $B$ and suppresses the autocatalytic reaction that requires two molecules of $B$. The front will have difficulty advancing here. In the region where $A$ protrudes into $B$, $A$ will react leading to advancement of the front. The net effect is to remove any initial non-planarity and give rise to a planar front.

If $D_B \ll D_A$, in regions where $B$ protrudes into $A$, rapid $A$ diffusion will lead to conversion of $A$ to $B$ leading to front advance. In regions where $A$ protrudes into $B$, small diffusion of $B$ into the $A$ region does not favour the autocatalytic conversion so the front will not advance rapidly here. Consequently, any small non-planarity will grow to make the front even more non-planar. Therefore, we expect that for some ratio of diffu-
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For $d = D_A/D_R > 1$, the planar front will lose its stability. An example of the front dynamics for $d = 5$ is shown in figure 1.14 where the minima in the front profile are plotted versus time. The resulting space-time plot shows the chaotic nature of the front dynamics. The (black) minima act like “particles” in the system: they move and when they collide they coalesce to form a single minimum. If the distance between two minima is too large a new minimum is formed. Thus, the average density of “particles” per unit length of the interface remains constant but the instantaneous number of “particles” fluctuates due to the creation and annihilation events for the minima.

In order to investigate such front instabilities quantitatively one may derive an equation for the profile $\phi(y,t)$ of the front directly from the reaction diffusion equation. This Kuramoto-Sivashinsky equation [69]

$$\frac{\partial \phi(y,t)}{\partial t} = \nu \frac{\partial^2 \phi}{\partial y^2} - \frac{v}{2} \left( \frac{\partial \phi}{\partial y} \right)^2 - \kappa \frac{\partial^4 \phi}{\partial y^4}$$  (1.16)

describes a number of general features of such front dynamics. The parameters $\nu$, $v$ and $\kappa$ may be related to the parameters in the original reaction-diffusion equation. The nonlinear term accounts for the fact the velocity of the front depends on its curvature, while the gradient terms arise from diffusive effects. The coefficient of the fourth-order gradient is positive while the sign of $\nu$ depends on the diffusion coefficient ratio $d$: for $d > d_c$, where $d_c$ is a critical value of $d$, $\nu$ changes from being positive to negative. This negative value of the “diffusion coefficient” leads to an instability whose growth is controlled by the stabilizing fourth-order term.
Instead of studying the full reaction-diffusion equation we may now explore the front dynamics directly through equation (1.16). This equation yields front dynamics like that described above.

In addition to flame fronts, which have been extensively studied experimentally, front instabilities have been investigated for the isothermal cubic autocatalytic iodate arsenous acid system [70] as well as for polymerization reactions where thermal and hydrodynamic effects lead to complicated front patterns. [71] Front instabilities also play a role in determining the labyrinth patterns seen in recent chemical experiments. [72]
1.6 Conclusion

Our understanding of the development of oscillations, multi-stability and chaos in well stirred chemical systems and pattern formation in spatially distributed systems has increased significantly since the early observations of these phenomena. Most of this development has taken place relatively recently, largely driven by development of experimental probes of the dynamics of such systems. In spite of this progress our knowledge of these systems is still rather limited especially for spatially distributed systems.

Several important topics have been omitted in this survey. We have described only a few of the routes by which chaos can arise in chemical systems and have made no attempt to describe in detail the features of the different kinds of chemical strange attractor seen in experiments. A wide variety of chemical patterns have been observed and while the many aspects of the the mechanisms for their appearance are understood, some features like nonlinear pattern selection still present challenges and new patterns continue to be discovered. An ubiquitous class of chemical patterns that was not discussed here are those that arise from diffusion limited aggregation (DLA). [73] Such DLA clusters are seen in many contexts including electrochemical deposition processes and are often analysed using the concepts of fractal geometry [10] and wavelets. [74, 75] Also, methods for controlling chemical chaos [76] have not been discussed in this chapter although they have potential applications for both industrial processes and biological systems.

In spite of these limitations it is hoped that this chapter will provide an introduction to the unusual phenomena that chemically reacting systems exhibit when driven far from equilibrium and an indication of how these phenomena may be analysed. Although such systems were often regarded as curiosities in the past, it is now clear that they are the rule rather than the exception in nature and deserve our full attention.
Conclusion

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Conclusion

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