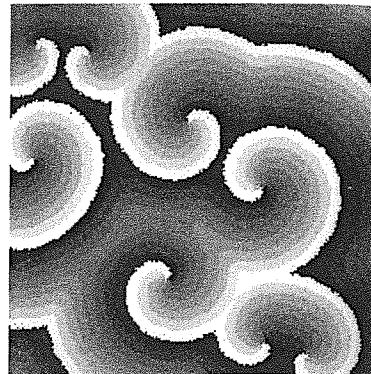


WAVES

A wave is but a single thing, we're told; but from its hue you'd think it was a mixture—flowers and snow!

Ki no Tsurayuki
The Toas Diary



Amongst the sprawling modern myth of Thomas Pynchon's *Gravity's Rainbow* is a fleeting reference to a man who tried to make patterned paint. The reference is clearly meant to document a quixotic, absurd ambition, for we all know that paint does not unmix into the separate pigments that went into its making.

But life is always stranger than we think. Take a look at Plate 4. Pynchon's ill-fated entrepreneur would have done well to follow the recipe that produced these blue and yellow stripes; for this is indeed a stable pattern that emerges spontaneously from a mixture of chemical compounds.

This brew of chemicals is just one of many that have been found to generate spatial patterns. Some of these, like that in Plate 4, are stationary; others are dynamic, releasing waves of colour to a pulse as regular as a clock's tick. Their crucial characteristic, however, is that the elements of the pattern—its symmetry, its length scale, its rhythms—are set not by any external agency but by the internal dynamics of the chemical system, by the rates at which the molecules react with one another and travel through the medium in which they are dissolved.

If you are surprised that a mixture of chemical compounds can form stripes or beat out a pulse, you are not being naive. Indeed, when rhythmic behaviour was observed in a chemical system in the 1920s, most chemists dismissed the observations out of hand as impossible. The idea seemed to contravene a physical law that scientists believed to be unassailable. I will relate in this chapter the tale of how chemical pattern formation has made the difficult journey from a contemptuously dismissed oddity to an exciting new field of research. It is a shame that the Russian biochemist Boris Pavlovitch Belousov did not live to see this story unravel. For initiating the field of dynamical pattern formation in chemistry, all Belousov got for his troubles during his lifetime was the derision of his peers.

Travelling waves

Off balance

Belousov had not intended to create such peculiar and controversial effects in his chemical reaction; rather, he had devised the mixture with the intention of mimicking some of the aspects of the metabolic biochemical process called glycolysis, in which the energy in glucose is liberated as enzymes break it down. He found, however, that this mix of compounds did not seem to settle down into a steady, equilibrium state. Instead, it kept changing colour with uncanny regularity, from clear to yellow and back again. I don't know if that will sound terribly surprising to anyone who has not studied chemistry, but you might get some indication of how this would once have seemed to a chemist if you imagine pouring cream into your coffee and finding it repeatedly dispersing to a uniform brown and then separating out again into a white swirl in the black liquid. Not just once (which would be odd enough), but again and again, at regular intervals.



There is a scientific way to express our intuition about such seemingly one-way processes, and it was the apparent violation of this principle that upset Belousov's contemporaries so much. All physical processes have a preferred direction, be they the way an apple falls from a tree to the ground, the way iron goes rusty or, indeed, the way cream disperses in coffee. The arrow of time is directed by the condition that the total entropy of the Universe—crudely speaking, its total amount of disorder—must increase. This is the second law of thermodynamics, which is the science of change.*

You can probably see that a uniform dispersion of particles of cream throughout a cup of coffee corresponds to a more disordered state than one in which some well-defined pattern of cream and coffee persists in the cup—the positions of the cream and the coffee are more randomized when the two are fully mixed. For the rusting of iron, or for any other chemical reaction, the direction of entropy increase is not so obvious, but it can be deduced readily enough by making measurements of the heat flow and pressure or volume changes during the reaction. The main point is that there *is* a preferred direction, a preferred equilibrium state. Reactions cannot go first towards one end-point and then back again, because in only one of these directions can entropy increase.

Or so the scientific establishment thought in 1951, when Belousov tried to publish his finding. After being snubbed by the journals to which he sent his papers, the Russian biochemist was forced eventually to publish the work in an obscure conference proceedings devoted to another topic entirely. Outside the Soviet Union, it remained virtually unknown.

Had Belousov only known about it, he could have taken some solace from the fact that others before him had anticipated, and even seen, oscillating chemical reactions—and been met with similar indifference or disbelief. In 1910 the mathematician Alfred Lotka published a paper describing a theoretical chemical reaction that underwent damped oscillations—the direction

changed back and forth in a periodic manner, but these changes gradually died out and the system settled into a steady state. In 1920 he showed that a related hypothetical reaction could sustain oscillations indefinitely. The Italian biologist Vito Volterra showed in the 1930s that Lotka's scheme could be used to model fluctuations in fish populations, since it turns out that the same equations that describe reacting chemicals can provide a crude description of interactions between a predator population and its multiplying prey population. I will return to this in Chapter 9.

Lotka's work made little impact on the chemistry community at the time. One of the few to appreciate its significance was William Bray of the University of California at Berkeley, who found in 1921 that a chemical reaction between hydrogen peroxide and iodate ions, which generates oxygen and molecular iodine, exhibits oscillations in the amount of these products generated over time. Even though Bray referred to Lotka's work in his own report, he was told the same as Belousov would be 30 years later—your claims violate the second law of thermodynamics, so they must be the result of poor experimental technique.

But during the 1960s, biochemist Anatoly Zhabotinsky, then still a graduate student of Moscow State University, began to take Belousov's results seriously. His careful experiments finally persuaded others that the effect was real. Zhabotinsky found a combination of compounds that generated a more pronounced colour change, from red to blue, by adding an indicator whose colour depends on the relative concentrations of metal ions involved in the reaction. In Appendix 2 I have given recipes both for this version of the reaction, which has become known as the Belousov-Zhabotinsky (BZ) reaction, and for a related oscillating reaction in which a colour change from yellow to blue is induced by the presence of starch, which turns blue when iodine is produced in the reaction. These are now called clock reactions, for obvious reasons (but don't set your watch by them).

By the end of the 1970s, the BZ reaction was an accepted and at least partly understood part of textbook chemistry, and in 1980 Belousov and Zhabotinsky (together with colleagues Albert Zaikin, Valentin Krinsky and Genrik Ivanitsky) were awarded the Lenin Prize for their discovery. But Belousov had died 10 years earlier, and so never saw his work reach wide acceptance and recognition.

How, though, can we reconcile the oscillatory behaviour with the second law of thermodynamics? Broadly

* In the previous chapter I suggested that the direction of change is determined by free energy, which must always decrease. This is entirely equivalent to the condition that entropy must increase, but is simply more convenient: free energy (the amount of mechanical work that can be extracted from a system) can be readily measured, whereas the total entropy of the Universe can't. The definition of free energy is in fact chosen precisely so as to make thermodynamics an experimentally accessible enterprise.



speaking, we just need a little patience—for the oscillations do not last for ever. If we leave it for long enough, a colour-changing beaker of the BZ mixture will at last settle down into a uniform and unchanging steady state. There is after all a stable equilibrium for the reaction, and it is one in which the overall entropy of the beaker's contents and their environment has increased, just as the second law requires. It is just that the mixture takes a strange and circuitous route in getting there.

The fact is that the second law, like all of the thermodynamics developed during the late nineteenth and early twentieth centuries, pertains only to equilibrium states. It speaks only of end-points. And those were, for a long time, all chemists were really interested in. From a certain perspective, this is understandable. If you are interested in making a particular chemical compound, the first thing to ask is whether it is thermodynamically possible—whether entropy will increase in transforming the starting materials to the end product. If the answer is no, you can forget about it.

But equilibrium is a dull place to be. Nothing happens there. If the Universe were itself at thermodynamic equilibrium, it would be a lifeless place pervaded by a uniform, dim glow of just a few degrees above absolute zero. Just about every phenomenon that interests us is an out-of-equilibrium process—life, to mention one. All human activity, from thinking to shopping to sleeping, takes place in a state that is far from thermodynamic equilibrium. However we may think we hanker after equilibrium in our lives, we tend to do all we can to avoid it in the truest sense, since genuine equilibrium is death.

Our planet is itself far from equilibrium. Why else would the weather be so unpredictable? The seas, the skies and the ground beneath us are all in constant motion, in a manner discussed further in Chapter 7. The atmosphere is a complex chemical brew whose relative constancy of composition is not at all an indication of a true equilibrium state. Rather, this composition is maintained *actively*, by cycling of carbon, oxygen and nitrogen and other elements between the air, living organisms and the geological environment. It is only because of the presence of life on Earth that our planet has the composition that it does: the non-equilibrium rhythms of life maintain an oxygen content that would be extremely peculiar on a dead planet. If aliens were ever inclined to monitor the Earth for signs of life, they'd have no need to look for cities, roads or radio transmissions—one glance at the composition of the atmosphere (something that can in principle be done light years away) would give the game away.

The theme of rich behaviour in systems out of equilibrium is one that will recur many times throughout this book—it is one of the unifying themes of pattern formation, and has been developed into a formal and exact science. For now, I wish to make a crucial point about such systems: they do not come for free, but need a supply of energy. Without this, they will decay—be it slowly or quickly—to a bland equilibrium.

All the same, there is a kind of magic in this transaction. You put in featureless, indiscriminate energy, and the out-of-equilibrium system uses it to organize itself into patterns that can astonish. This is not quite form for free, but it is nevertheless form from formlessness.

To maintain the out-of-equilibrium processes of life and of our planet's shifting meteorology and climate, the energy comes almost entirely from the Sun, in the form of heat and light. A little comes from the planet's hot interior, energy from radioactive decay or left over from the fiery process of planet formation four-and-a-half billion years ago. To sustain indefinitely the oscillations of the BZ reaction, we also need a source of energy. In practice this supply can take the form of a constant throughput of reactants and products: the reaction can be conducted in a stirred vessel in which fresh reactants are constantly supplied and end products withdrawn. Such vessels are called continuous stirred-tank reactors (CSTRs). Living organisms can be considered as approximations to CSTRs insofar as they (we) continually (though perhaps not continuously) ingest food (fresh material for metabolism) and excrete waste products. In this way we sustain our out-of-equilibrium (and sometimes oscillatory) biochemistry.

There is, then, no reason to fear for thermodynamics in the BZ reaction. But how is it that the reaction keeps changing its mind while it remains far from equilibrium? To answer that, we need to look at a bit of real chemistry.

The chemical seesaw

The key to the BZ reaction is the chemical process known as catalysis, in which some chemical compound speeds up the rate of a chemical reaction without itself being changed by the process. The majority of industrial chemical processes use some kind of catalyst to accelerate product formation—otherwise, the reactions would be too slow to be economically viable. And almost all biochemical reactions in the body are mediated by natural protein catalysts called enzymes.

A catalyst interacts with the reacting molecules so as to help them become transformed. When special tech-



niques are used to see the intermediate steps in a catalytic reaction, we find that the catalyst is not at all aloof from the action—while the reaction remains out of equilibrium, it might take on a new, ephemeral structure, but once the reaction has gone to completion, the catalyst is reformed as if untouched.

What makes the BZ reaction different from most catalytic reactions is that it makes its own catalyst. That is to say, one of the product molecules acts as a catalyst to speed up the formation of more product. This is an example of a positive feedback process, and left to its own devices it will simply make things go faster and faster. A nuclear explosion is also an example of positive feedback, as indeed are most chemical combustion and explosion processes, and all demonstrate that this kind of self-catalysis, or *autocatalysis*, literally blows up out of control.

Clearly the BZ reaction does not blow up out of control, and the reason for that is that there is a competing process that kicks in to stop the autocatalytic reaction from going to completion (that is, reaching equilibrium). Because of the positive feedback, an autocatalytic process tends to use up its supplies very quickly—even in a CSTR, it consumes the reactants faster than they can be provided. So the concentration of reactants in the vessel plummets, and the concentration of products surges. Since one of these products is coloured, the mixture of chemicals takes on that colour.

Once the concentration of reactants gets low enough, the autocatalytic process runs out of steam, and this allows the competing reaction (which is not autocatalytic) to take over, and the mixture starts to generate a different product, with a different colour. In time, this process too consumes nearly all of its starting materials, and the autocatalytic process kicks back in. Crucially, each of these two processes regenerates some of the compounds needed to get the other started. So while one reaction holds sway, it is paving the way for the other to take over.

Deducing the various steps of the BZ reaction proved to be a complicated and difficult task, since they involve at least 30 different chemical species. Most Western scientists first learned about the BZ reaction in 1968 at an international symposium in Prague, and by 1972 Richard Field, Endre Körös and Richard Noyes at the University of Oregon had put together a somewhat simplified model for the reaction mechanism, which still retains its essential characteristics. Two years later, Field and Noyes pared down this model to an even simpler one, dubbed the Oregonator, in which there are just five

distinct steps and six different chemical species. I outline this scheme in Box 3.1; I don't think you'll find that any great knowledge of chemistry is required to follow it, but because I know how readily some people's eyes glaze over at the sight of chemical formulae of any sort, I shan't inflict it on the main text. For what comes later, you'll simply need to know the following.

The reaction has two branches, A and B: on each branch, a chemical reaction converts certain electrically charged chemical species (ions) to others. The change in colour between blue and red signifies a switch from one branch to the other—a change-over in predominance of the chemical processes taking place. The 'input' to the reaction (the raw material, as it were) is bromate ions, denoted BrO_3^- . The 'output' (the end product) is BrO^- ions. So to sustain the oscillations indefinitely, we need to keep feeding the system with BrO_3^- and removing BrO^- .

We can see the oscillations visibly because of the colour change; but it is often more useful to depict them in terms of the changes in concentration of the various intermediate ions in the reaction—the ones that come and go as BrO_3^- gets consumed and BrO^- produced. One such is the bromide ion, denoted Br^- . Initially, the concentration of bromide in the mixture is high. As Branch A proceeds, the concentration falls, and it is this decline that eventually allows Branch B to take over. But subsequently, another reaction (eqn 3.5) boosts the concentration of Br^- back up again. Plotted as a graph, we see these variations as a series of regular oscillations (Fig. 3.1). Because of this periodicity in time, Arthur Winfree of the University of Arizona calls the BZ reaction a 'time crystal'. (Note, however, that there is an initial 'induction period' before the mixture settles down to regular oscillations.)

Meanwhile, the concentration of another intermediate ion, BrO_2^- , also rises and falls, with the same periodicity as the concentration of Br^- but with the

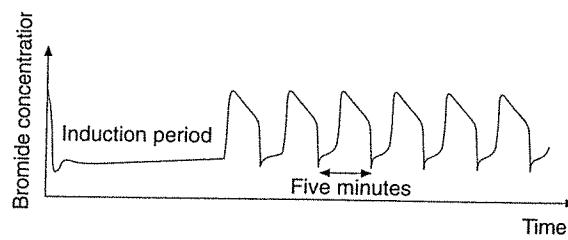


Fig. 3.1 The oscillations of the Belousov–Zhabotinsky reaction can be revealed by monitoring the concentration of bromide ions in the mixture, which rises and falls periodically through time.

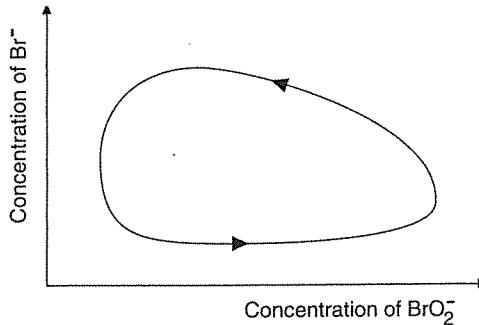


Fig. 3.2 Another way to portray the chemical oscillations is to plot changes in the concentration of one substance (say bromide Br^-) against another (BrO_2^-). This plot traces out a closed loop, called a limit cycle.

peaks out of step. This is because the production of BrO_2^- is greatest while Branch B holds sway, whereas the concentration of Br^- is greatest just before the switch back to Branch A. One way of depicting both of these rising and falling concentrations at the same time is to plot one against the other (Fig. 3.2). What we see is a closed loop: as time progresses, the concentrations trace out a repetitive circuit of the loop. The reaction will typically be initiated from a point on the graph that lies off the loop, but is quickly drawn onto it—this transient pathway onto the closed loop corresponds to the induction period in Fig. 3.1.

The loop is called a limit cycle, and is a robust characteristic of the reaction. That is to say, for a given set of conditions (temperature and flow rate in the CSTR), any initial point in the plot of the two concentrations will be drawn onto the limit cycle, and the subsequent evolution of the system will be restricted to an endless circulation of the loop, so long as the conditions remain unaltered. You could, if you like, regard the limit cycle as a kind of robust ‘form’ that the BZ reaction takes in this abstract mathematical space. These stable forms are called *attractors*.

Going places

The oscillating BZ reaction thus has a characteristic pattern of sorts, as depicted by the oscillations in Fig. 3.1 or the limit cycle of Fig. 3.2. But these are patterns in time, whereas on the whole I shall be talking in this book about patterns in space—the kind of pattern that you can see at a glance. The BZ reaction can generate these too. The intricate spatial patterning of the BZ reaction was the second shock it held in store for theorists; says Arthur Winfree, ‘Its antics turn out to resemble nothing

foreseen in the thirty years devoted to the subject by theoretical chemists and biologists’.

Above I have considered only the case of a well-mixed reaction, in which an automatic stirring device ensures that the concentrations of the component species, while varying in time, remain uniform at any instant throughout the reaction vessel. But if the reaction is carried out without stirring, there will inevitably be small variations in concentrations from place to place. This is true for any unstirred chemical reaction, but in general it doesn’t lead to anything remarkable—the rate of the reaction (which usually depends on the concentrations of some or all of the reactants) then simply varies slightly from place to place too.

For the BZ reaction, however, small variations can make a big difference. This is because the reaction has an autocatalytic component: the positive feedback inherent in this process has the effect of blowing up minor differences into major ones. It means, in particular, that some regions of the mixture can be flipped onto one branch while others remain on the other branch. We then find a mixture in which the colour varies from place to place.

These colour variations do not take the form of a random patchwork of red and blue. Rather, we see complex patterns of astonishing beauty: in a shallow dish of the BZ mixture, concentric rings or twisting spirals of red and blue are produced, which radiate outwards like ripples. The chemical oscillations take the form of travelling chemical waves (Fig. 3.3 and Plate 5).

These patterns were first described by the German scientist H.G. Busse in 1969, although their true nature as chemical waves was perceived the following year by Zhabotinsky and his colleague Albert Zaikin. The pat-

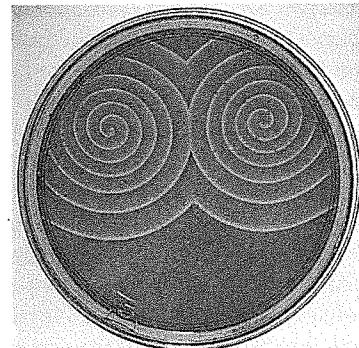


Fig. 3.3 Spiral waves in the unmixed BZ reaction. The waves continuously expand and collide. (Photo: Art Winfree, University of Arizona.)

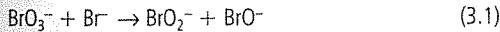


Box 3.1: The Oregonator

If the BZ reaction is allowed to go to completion (to reach thermodynamic equilibrium), the overall process is one in which an organic compound, malonic acid, is converted to a bromine-containing variant, bromomalonic acid, by reaction with bromate ions, BrO_3^- . (Here the chemical formula connotes that the ion—a negatively charged molecule—contains one bromine atom and three oxygen atoms.) This process is catalysed by certain metal ions, either doubly charged iron (Fe^{2+}) or triply charged cerium (Ce^{3+}).

But curiously, the Oregonator model does *not* trouble itself at all with the conversion of malonic acid—this compound does not feature amongst the six involved in the reaction scheme. This is because the Oregonator is a description of the non-equilibrium states of the reaction, those states that flash alternately red and blue, whereas the malonic acid enters into the scheme only once all the interesting autocatalysis has gone through its paces, and is spat out of the end (in brominated form) as a dull product of the overall equilibrium.

This transformation is the end product of the *non-autocatalytic* branch of the scheme. The Oregonator includes this branch only up to an earlier stage in the full sequence of transformations. The initial reactants on this branch are BrO_3^- ions and bromide (Br^-) ions, both present in the general recipe (Appendix 2). These ions react to generate the ions BrO_2^- and BrO^- :



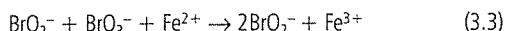
If the chemical formulae look daunting here, just bear in mind that all equation 3.1 is showing is the transfer of an oxygen atom from BrO_3^- to Br^- . The next step on this branch involves a reaction between the BrO_2^- produced in equation 3.1 and more Br^- :



Again, just think of this as the transfer of an oxygen atom from BrO_2^- to Br^- . It's the BrO^- produced in these steps that ultimately goes on to convert malonic acid to bromomalonic acid, but we don't need to worry about that.

Now, the rate at which these two transformations occur depends on the concentration of the reactants (the compounds on the left-hand side of the arrow). Simply speaking, the more there are of these around, the better are their chances of encountering one another and reacting. So initially, when there is a lot of Br^- in the mixture, the rate is fast. But as the Br^- gets consumed, the rate starts to decline.

That is when the second, autocatalytic branch of the Oregonator comes into play. For it happens that BrO_2^- ions, produced in equation 3.1, can react with BrO_3^- (one of the initial reactants, remember) to generate two molecules of BrO_2^- . This reaction can take place only in the presence of the metal ions (Fe^{2+} or Ce^{3+})—the function of these ions is to donate an electron (a negatively charged particle) to the reaction, which leaves them with an extra positive charge. So the metal ions get converted to Fe^{3+} or Ce^{4+} , respectively:



You might notice that this reaction doesn't quite add up—there are five oxygen atoms on the left-hand side but just four on the right. It is bad practice to write down 'unbalanced' equations like this, but I hope you'll excuse it—I've done so to keep things simple. In practice the extra oxygen is taken up by hydrogen ions (H^+) to make water (H_2O). The important thing to notice is that two BrO_2^- ions are produced from one. This is what gives rise to the autocatalysis, because the rate of the reaction depends on the concentration of BrO_2^- (it appears as a reactant on the left-hand side). As the reaction progresses, more and more BrO_2^- is produced, so the reaction goes faster and faster.

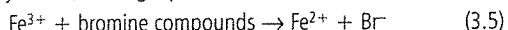
The BrO_2^- produced in equation 3.3 goes on, however, to react further—two of these ions exchange an oxygen atom:



Now we can see how, out of equations 3.1 to 3.4, oscillations in the concentration of chemical species in the mixture arise. Equations 3.1 and 3.2 comprise the first branch of the Oregonator scheme—call it Branch A. Initially, this reaction proceeds through to the completion of equation 3.2, which ultimately results in the formation of bromomalonic acid. The cocktail of BZ reagents includes an indicator that turns red in the presence of Fe^{2+} ions, and because these are added to the initial mixture (although they do not partake in Branch A), the mixture starts off red.

You can see that equation 3.1 produces BrO_2^- , which could in principle react with the BrO_3^- as in equation 3.3. But it turns out that BrO_3^- reacts faster with Br^- (eqn 3.1) than with BrO_2^- (eqn 3.2), so the former dominates. Eventually, however, the concentration of Br^- falls so far—because it is consumed in equations 3.1 and 3.2—that the rate of equation 3.1 slows down significantly. Then equation 3.3 has a chance to take over. Once it does so, Branch B (eqns 3.3 and 3.4) rapidly come to dominate, because equation 3.3 is autocatalytic. Moreover, it converts Fe^{2+} to Fe^{3+} , and the indicator turns blue in the presence of the latter.

If this were all there is to the Oregonator, we'd get just one oscillation—a switch from blue to red. But there is a final step, which switches the conditions back to those that favour the dominance of Branch A. In this step, a rather complex set of reactions between Fe^{3+} and other bromine-containing compounds results in the formation of both Fe^{2+} (turning the indicator red again) and plenty of Br^- (allowing equation 3.1 to reassert itself):



(I've left this equation so vague that you can't tell if it's balanced or not, again for the sake of simplicity.)

Equation 3.5 completes the Oregonator, and allows the reaction to flip back from Branch B to Branch A. Then the whole cycle repeats itself. To sustain the oscillations in a CSTR, we need to keep supplying BrO_3^- and removing BrO^- —you'll notice that the latter appears only as a product on the right-hand side of the reactions, whereas all the other species appear as both reactants and products.



terns are, as we shall see, not unique to the BZ reaction but are generic to a whole class of non-equilibrium systems in chemistry and beyond. They can be captured most easily in a BZ mixture by infusing it into a gel, which slows down the rate at which the chemical species can diffuse through the medium and so stabilizes the chemical waves. The patterns are clearly an example of symmetry breaking: the uniform reaction medium breaks up into complex structures that manifest a degree of organization in space and time. I explain how to create them in Appendix 3.

We can imagine readily enough that a fluctuation in the relative concentrations of the reacting species might shift the reaction from Branch A (red) to Branch B (blue). But why then does this disturbance radiate outwards as a wave with a specific period?

As the autocatalytic cycle of Branch B takes hold, its influence spreads into the surrounding medium and the blue region expands from its origin. But as the wavefront advances, the cycle is played out behind it: the Fe^{3+} produced by equation 3.3 partakes in equation 3.5, regenerating the Fe^{2+} and Br^- needed for Branch A. In effect, the red regions to either side of the wavefront are then no longer equivalent: beyond the wavefront, the medium is ripe for 'colonization' by Branch B, whereas behind the wavefront this branch has run itself to exhaustion and Branch A has begun a new cycle, which is completed when the next wavefront arrives.

This non-uniform BZ mixture is what physicists call an *excitable medium*. Such a medium can change its state locally—switching from the red Branch A to the blue Branch B, for instance—when some stimulus (here the concentrations of chemical species conducive to sparking off Branch B) reaches a certain threshold. But, crucially for formation of these complex patterns, the medium goes through a 'refractory' period once it has been excited. During this time, it cannot be excited again. It is this refractory period that enables steady, periodic oscillations to be set up, giving rise to intricate spatio-temporal patterns.

This mechanism accounts for the target patterns; but what is happening with the spirals? These are basically a mutation of the targets, generated by a perturbation to the expanding circular waves. Such perturbations can happen by accident if, for example, the wavefront encounters some obstacle in the reaction medium; or they can be introduced on purpose, for instance by blowing air onto the wavefront through a pipette. Disturbances like this might break apart the circular wavefront, and the fragmented ends become 'rotors'—

rotating centres of excitation from which the arm of the spiral wave emanates (Fig. 3.4a). Because a broken wavefront must have two ends, spiral waves are commonly formed in pairs that rotate in opposite directions. German chemists Stefan Müller and O. Steinbock have shown that a laser beam can be used to marshal several rotors together to create multi-armed spirals in a modified BZ reaction mixture that is sensitive to light (Fig. 3.4b).

I explained in the first chapter that one of the goals of studies in pattern formation is to reduce a pattern-forming system to its bare essentials, so that we can start to see which patterns are universal—characteristic of certain classes of systems rather than dependent on the fine details. For the BZ reaction, even the simplified

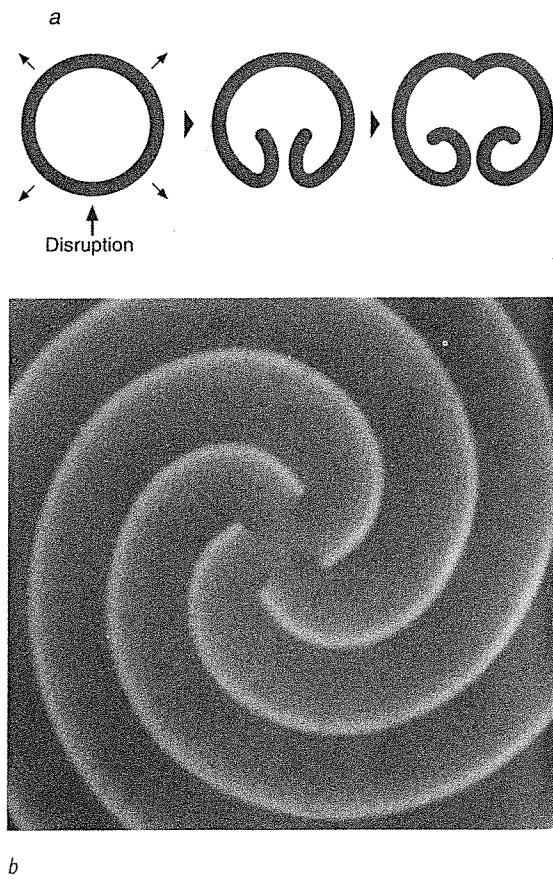


Fig. 3.4 (a) Spiral waves develop in the BZ reaction from a disturbance that breaks up a circular wavefront of the target pattern. The two broken ends curl into counter-rotating spirals. (b) Multi-armed spirals can be created by bringing several rotors together. (Photo: Stefan Müller, University of Magdeburg.)



Oregonator scheme is quite a complicated one to deal with mathematically, although Richard Field and co-workers have subsequently managed to concoct a theoretical scheme that includes just three independent variables rather than the six concentrations of chemical species in the original Oregonator, while still capturing most of the essential behaviour. But to model a non-uniform BZ medium using one of these chemical schemes, with their menagerie of mutually interacting compounds, is a highly computer-intensive task that would not tell us much about the *universality* of the patterns formed.

It is possible to reproduce these patterns, however, in a model that includes no chemistry whatsoever. In this model the flat reaction medium is represented by a two-dimensional checkerboard lattice of little compartments or cells, each of which interacts with those around it. To model the properties of an excitable medium, each cell can exist in three states: *receptive* (meaning that it is liable to become excited), *excited*, and *refractory* (which means that it is recovering from a period of excitation). When in the excited state, the cells deliver a stimulus to those around it. If any receptive cell receives a sufficiently large stimulus from its neighbours (equivalent, in the BZ reaction, to receiving a certain influx of diffusing chemical species of a certain type), it too becomes excited. But once excited, a cell eventually enters the refractory state, during which time it remains unresponsive to stimuli regardless of what its neighbours are up to.

This kind of model is called a cellular automaton, reflecting the fact that the cells are mindless and respond to stimuli in a kind of automatic, knee-jerk way. Cellular automata were devised in the 1950s by mathematicians John von Neumann and Stanislaw Ulam, who were interested in modelling self-reproducing entities; I will say more about them in Chapter 9. For now it is enough to say that they represent a very general, computationally tractable way to model complex interacting systems. The behaviour of the system as a whole depends on the rules that govern the interactions between neighbouring cells. In the case of the cellular excitable medium, travelling spiral and target patterns arise when excitations are initiated at a few points (Fig. 3.5). Moreover, the wavefronts annihilate each other in just the same way as they do in the BZ reaction. Because these patterns are formed without including any ingredients of the specific chemical reactions taking place, we should expect them to be characteristic of *any* medium that is excitable. Notice

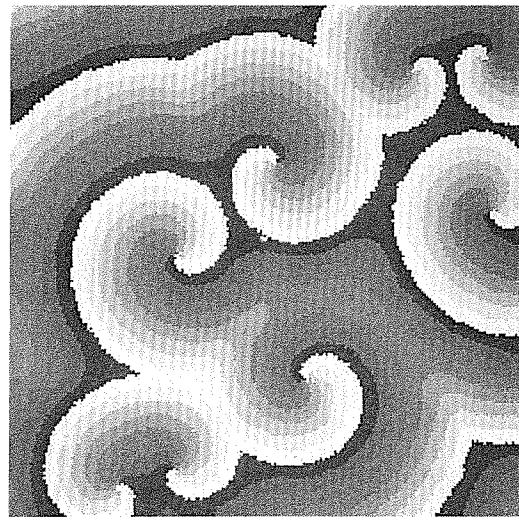


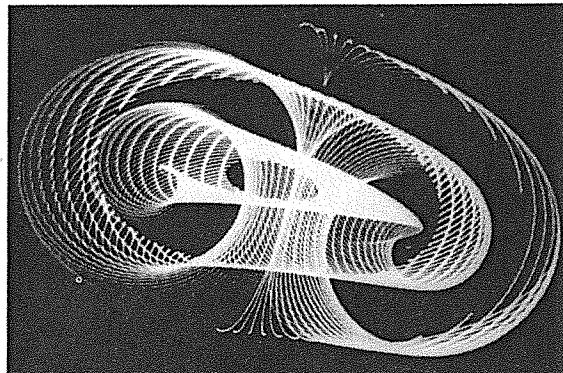
Fig. 3.5 The wave patterns of the BZ reaction can be mimicked by a model that takes no account of the chemical specifics, but simply presents the reaction medium as a lattice of cells that can be excited by receiving stimuli from their neighbours. (Images: Mario Markus and Benno Hess, Max Planck Institute for Molecular Physiology, Dortmund.)

too that the cellular automaton model does not include any description of the *oscillatory* nature of the BZ reaction; rather, it is the *excitable* nature of the reaction medium that creates the spatial patterns.

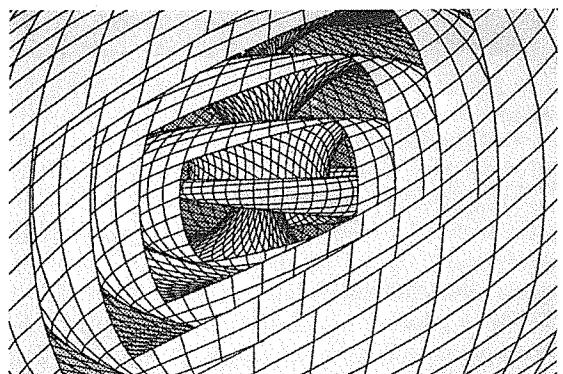
I've talked so far about BZ mixtures in thin layers, which are essentially two-dimensional. In three dimensions the patterns become more complex. The simplest is a scroll wave, in which a two-dimensional spiral wave is drawn out into a kind of curled-up scroll (Fig. 3.6a). The question naturally arises of what happens at the ends of a scroll, and the answer is that commonly they join up to form a *scroll ring*. Cross-sections of a scroll ring in the plane of the ring look like concentric circles—target patterns—while those perpendicular to the ring appear as spiral waves curling in opposite directions. Scroll rings have been seen in the laboratory in BZ media since the 1970s. Arthur Winfree and co-workers have made theoretical investigations of more complicated scroll rings in which the scroll acquires a twist around the ring: this leads to complex patterns of wavefront collision and annihilation (Fig. 3.6b).

Frontal assault

There's an important refinement to be made in the relation between a chemical *travelling wave* and the pulsating target and spiral patterns of the BZ reaction.



a



b

Fig. 3.6 The patterns in a three-dimensional BZ mixture are more complex. One of the simplest, the analogue of a two-dimensional spiral, is the scroll wave (a), which can curl up on itself to form a scroll ring. Twisted scroll rings have more complicated structures (b). (Images: Arthur Winfree, University of Arizona.)

Periodic pulsations can arise only in a medium that is *excitable*, but a propagating wavefront is a rather more common beast, something that could arise for instance from a single, one-off disturbance.

The idea that chemical reactions can develop travelling waves goes back a long way—before, even, the theory of oscillating reactions (which, as we saw, started with Lotka in 1910). At a meeting of German chemists in Dresden in 1906, Robert Luther, director of the Physical Chemistry Laboratory in Leipzig, presented a paper on the discovery and analysis of propagating chemical wavefronts in autocatalytic reactions. Sceptics were apparently quelled by Luther's demonstration of the phenomenon before their very eyes—he showed

chemical waves in a reaction between oxalic acid and permanganate ions, projected onto a screen in front of the audience.

Luther suggested that the waves arose from a competition between an autocatalytic reaction and the process of diffusion that transports the chemical reagents through the reaction medium. Diffusion is a random process—molecules of the reacting molecules are buffeted from all directions by collisions with molecules of the surrounding solvent (generally water), and as a result they execute a convoluted, meandering path often likened to a drunkard's walk. Despite this randomness, the molecules do actually get somewhere rather than just meandering a little around their initial positions—but the direction they take is random, and the distance travelled from some initial location increases only rather slowly as time progresses. (Whereas the distance covered by walking along a straight path at constant speed increases in direct proportion to the time elapsed, the distance travelled by a random walker is proportional to the square root of the elapsed time.) Random walks owing to diffusion were much studied at the beginning of the century, notably by Albert Einstein.

When a chemical reaction is conducted under conditions where the concentrations are not maintained uniformly throughout the medium by vigorous mixing, diffusion becomes important, since it limits the rate at which a reagent that has become used up in one region can be replenished from elsewhere to sustain further reaction. This is particularly important for autocatalytic reactions, since they can use up a reagent locally at an extremely rapid rate. If diffusion cannot keep pace with this, the reaction runs into problems. This is precisely the situation that I described earlier—although not quite in these terms—in the vicinity of a wavefront in the BZ reaction. The inadequacies of diffusional transport create the refractory period in the medium just behind an advancing wavefront, where the reaction has exhausted itself but has not yet been replenished with fresh reagents. The poorly mixed BZ reaction is thus an example of a so-called *reaction–diffusion system*, which is now clearly recognized as one of the most fertile generic pattern-forming systems that we know of.

After Luther's pioneering studies, the theory of reaction–diffusion systems was placed on a firm mathematical footing by the eminent population biologist Ronald Fisher and by the Russian mathematician Andrei Kolmogoroff and co-workers, both of whom published seminal works in 1937. Fisher was interested



in reaction-diffusion processes for modelling the spread of an advantageous gene in a population, not with their manifestation in chemistry—a curious repetition of Volterra's assimilation of Lotka's ideas on oscillating chemical reactions into mathematical biology earlier in the century. It is almost as if chemists were for decades unwilling to face up to the existence of these complex and surprising phenomena in their own field!

All the same, studies of waves in chemical media were conducted in parallel with, but independently from, work on oscillatory reactions since the beginning of the century. In 1900 the German physical chemist Wilhelm Ostwald described travelling pulses in an electrochemical system. When he used a zinc needle to prick the dark coating of oxidized iron on the surface of an iron wire immersed in acid, Ostwald saw a colour change that propagated away from the point of contact at high speeds. From the 1920s onwards, many researchers studied this simple system as an analogue of nerve impulses (which are also propagating electrochemical waves), and in the early 1960s Jin-Ichi Nagumo and co-workers in Tokyo observed spiral waves on the surface of a two-dimensional grid of iron wire subjected to this treatment. But this work, published in Japanese, met the fate so common for studies that are not reported in the English language—it was ignored in the West, until Zhabotinsky's efforts had established the significance of this sort of wave activity.

The ripples spread

The BZ reaction is by no means unique: several other chemical mixtures share the same general features of autocatalysis, feedback and competing reactions that lead to excitable and oscillatory behaviour. It has been seen too in many biochemical processes, including, rather pleasingly, the glycolytic cycle of metabolism that Belousov had first set out to emulate. Similar effects crop up in some corrosion and combustion reactions. When these processes take place in poorly mixed conditions, spatio-temporal patterns can arise whose forms are attractively diverse.

One of the functions of a catalytic converter in automobiles is to reduce emissions of carbon monoxide (CO), a poisonous gas, in the exhaust fumes. This is done by combining CO with oxygen gas in the converter to create carbon dioxide (CO₂), a reaction that is

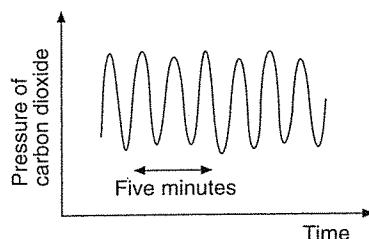
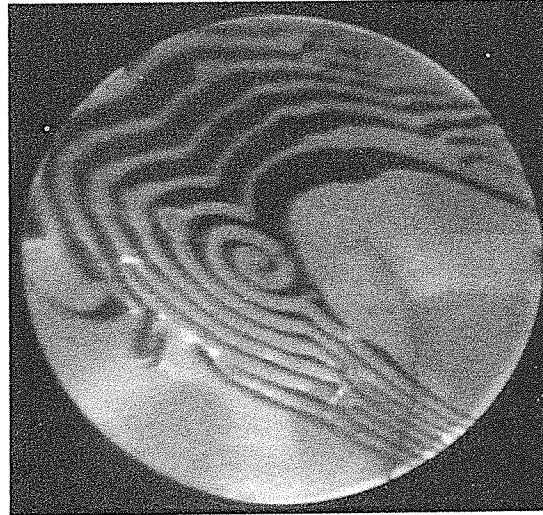


Fig. 3.7 Oscillations in the reaction of carbon monoxide and oxygen on a platinum surface. The reaction produces carbon dioxide.



a



b

Fig. 3.8 Target (a) and spiral (b) waves in the reaction of carbon monoxide and oxygen on platinum. The images are all several tenths of a millimetre across. (Photos: Gerhard Ertl, Fritz Haber Institute, Berlin.)



speeded up by the use of a metal catalyst consisting of a mixture of rhodium and platinum. The reaction takes place on the metal surface, where the chemical bonds in the reactant molecules are broken or loosened up. So the reaction between CO and oxygen on a platinum surface is of considerable technological interest. There is no obvious mechanism for *autocatalysis* here, however—the product is simply CO_2 , which is not then involved in subsequent reactions.

So it was a surprise to Gerhard Ertl and colleagues at the Fritz Haber Institute in Berlin when they found oscillatory behaviour in the rate of this reaction in 1985 (Fig. 3.7). And when in the early 1990s the Berlin group developed a new kind of microscope to look at the way that the CO and oxygen were distributed on the surface, they saw spiral and target patterns just like those of the BZ reaction, albeit just a fraction of a millimetre across (Fig. 3.8). The bright regions in this figure correspond to parts of the metal surface covered with CO molecules, and the dark regions are richer in oxygen atoms. Ertl's team deduced that the molecules of CO that became stuck to the metal surface were altering its structure, and thereby its catalytic behaviour, in a way that introduces feedback into this apparently simple reaction.

Platinum metal is a crystal: its atoms are packed together in a regular array like oranges on a fruit stall. On a clean platinum surface exposed by cutting through the metal, the arrangement of atoms depends on the angle at which the cut is made; for one particular cleavage plane, the surface looks like that in Fig. 3.9a. This is called the $\{110\}$ surface, and the arrangement of surface atoms is termed the (1×1) phase. In a vacuum, the top-most atoms of a freshly exposed platinum (1×1) surface will spontaneously shift their positions to create a different surface structure with a lower surface energy. This is called the (1×2) phase, and has a 'missing' row of surface atoms (Fig. 3.9b). The rearrangement process is called a surface reconstruction.

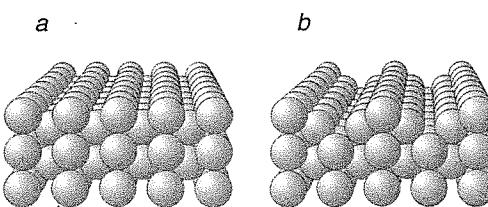


Fig. 3.9 (a) The atomic structure of the 1×1 surface phase of platinum. (b) In a vacuum, this surface will rearrange itself to the 1×2 reconstruction.

If CO molecules become attached to the reconstructed (1×2) surface of platinum, the balance of energies gets shifted around, and the original (1×1) phase becomes more favourable. This means that, as the reaction between CO and oxygen atoms on the platinum $\{110\}$ surface proceeds, the surface does not remain passive but shifts its structure between the (1×2) and (1×1) phases, depending on the amount of CO on the surface.

Now the point is that these two surface phases have different catalytic abilities: the (1×1) phase is considerably better at speeding up the reaction with oxygen than is the (1×2) phase. We can now see the possibility of some subtle and complex interactions, which can give rise to feedback. The more the bare (1×2) surface becomes covered in CO, the greater the extent of reconstruction to the (1×1) phase and the more the catalytic potential of the metal is enhanced. But as the reaction proceeds, the CO gets converted to CO_2 , which departs from the surface and leaves behind a bare (1×1) surface. On its own, this prefers to revert to the reconstructed (1×2) phase.

Gerhard Ertl, David King at Cambridge University, and their co-workers have devised a six-step reaction scheme that is akin to the Oregonator of the BZ reaction, which incorporates these various processes for reactions on platinum surfaces. It includes an autocatalytic process in which the reaction between CO and oxygen on the (1×1) surface creates new 'bare' catalytic sites. They have found that this scheme produces oscillatory behaviour of the various reaction parameters, such as the rate of CO_2 formation or the surface coverage of CO (Fig. 3.10). Like the Oregonator, the process jumps between two branches—essentially a low-reactivity branch involving the (1×2) surface and a high-reactivity branch involving the (1×1) surface—with the autocatalytic steps providing a mechanism for rapid switching between the branches. It is easy to see that sites of non-uniformity in these surface reactions can act as the centres for the formation of travelling waves like those shown in Fig. 3.8.

Several other metal-catalysed surface reactions are now known to show oscillatory behaviour. One difference between these essentially two-dimensional processes and those in flat dishes of the BZ mixture is that for the latter the medium is *isotropic*: it looks the same in all directions. For surface reactions taking place on metal crystals, on the other hand, all directions are not the same, because the metal atoms are lined up in a regular checkerboard-like array. This means that the

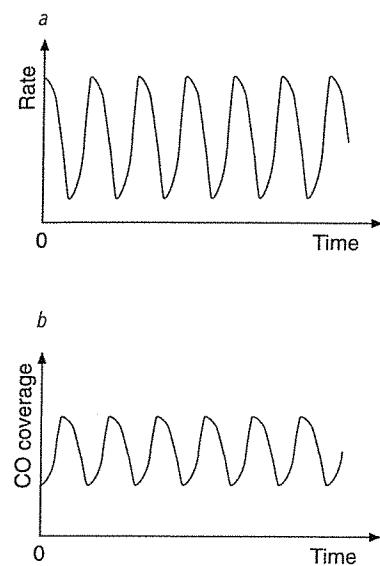


Fig. 3.10 The oscillations in the surface reaction of CO and oxygen can be reproduced by a theoretical model that includes the autocatalytic processes. Oscillations are seen in both the rate of reaction (a) and the amount of carbon monoxide on the surface (b).

ability of the reacting molecules to move about can be similarly anisotropic (direction-dependent). It is for this reason that the target and spiral patterns in Fig. 3.8 are elliptical rather than circular—the speed of the chemical wave fronts differs in different directions. In extreme cases, this anisotropy means that the symmetry of the underlying metal crystal surface can leave itself

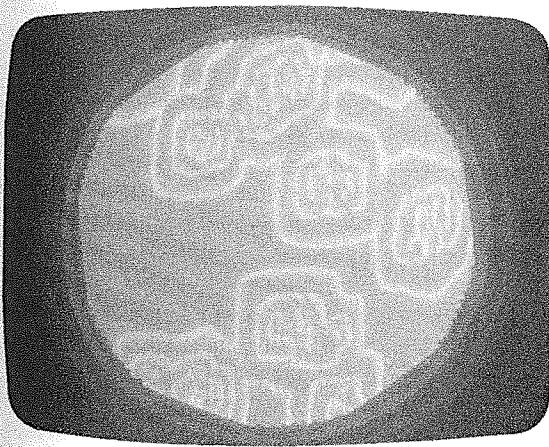


Fig. 3.11 The spiral waves of the oscillatory reaction of nitric oxide and hydrogen on a rhodium surface have a square appearance, which derives from the square symmetry of the underlying atomic lattice. (Photo: Ronald Imbihl, Fritz Haber Institute, Berlin.)

imprinted on the spatial patterns that arise. For example, Ertl's colleague Ronald Imbihl has seen square travelling waves in the reaction of nitric oxide and hydrogen on a rhodium surface, an echo of the square symmetry of the metal crystal surface (Fig. 3.11).

Rock art

If you are a rock collector, the target patterns in Plate 5 may look familiar. They are reminiscent of the stunning concentric bands displayed by agates (Plate 6). Agates are formed when water from rain or snow permeates through fissures in cooling basaltic lava, dissolving metal ions as it goes. Once the body of lava has cooled sufficiently, the ions precipitate out of the mineral-rich solution as agates. This is a process of crystallization occurring far from equilibrium, and so we should perhaps not be too surprised that it can lead to pattern formation.

Periodic patterns due to non-equilibrium crystallization and precipitation have a history that predates the discovery of oscillating chemical reactions. In 1896, the German chemist Raphael Eduard Liesegang performed experiments in which he reacted silver nitrate with potassium chromate in a gelatin gel. This reaction generates insoluble silver chromate, which precipitates as a dark deposit. In solution, this precipitate would all be flushed out at once, as the two salts would mix very quickly. But in a gel, the mixing is much slower, limited by the slow diffusion of the ions. Liesegang saturated the gel with potassium chromate, and then allowed a drop of silver nitrate solution to diffuse through it. He found that the dark precipitate appears in a series of rings behind a reaction front that advances through the reaction vessel. Many other chemical reactions that generate an insoluble compound show the same behaviour when limited by diffusion through a gel (Fig. 3.12), and you can try it for yourself using the recipe in Appendix 4.

Liesegang's experiments are not nearly so obtuse as they might sound. The precipitation of silver metal and salts in gelatin gels became a subject of intense interest in the late nineteenth century owing to its relevance to photography: black-and-white photographic emulsion is essentially a gel containing a silver salt, which is converted to a dark, fine precipitate of silver metal on exposure to light. Indeed, Liesegang's father and grandfather were both early pioneers of photography. Raphael Liesegang himself was by all accounts a remarkable, not to say eccentric, character, with interests every bit as catholic as D'Arcy Thompson's. He

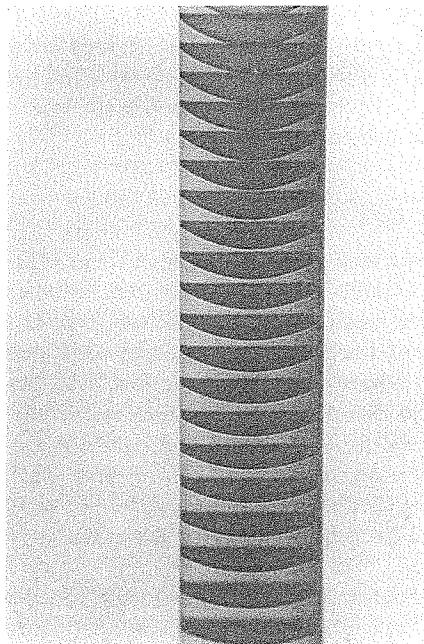


Fig. 3.12 Liesegang bands, a signature of oscillatory precipitation at an advancing diffusion front. Here the bands are produced by cobalt hydroxide as hydroxide ions diffuse down a column of cobalt-laden gelatin. (Photo: R. Sultan, American University of Beirut.)

wrote about the possibility of television in 1891 and, as well as his work on photography, he pursued research on bacteriology, chromosomes, plant physiology, neurology, anaesthesia and the disease of silicosis.

Liesegang's rings (only later was the reaction performed in cylindrical test tubes, so that the precipitation fronts appeared instead as a series of band-like disks) captured the imagination of many of the leading scientists of the time, including Lord Rayleigh, J.J. Thompson and Wilhelm Ostwald. Some early enthusiasts around the turn of the century suggested that in the bands and rings one might be seeing a simplified version of the stripes of tigers and zebras or the patterns on butterfly wings. In this, remarked one critic in 1931, 'enthusiasm has been carried beyond the bounds of prudence'. But as we will see in the next chapter, on one level at least such scepticism is misplaced (although given what was known at the time about chemical pattern formation—next to nothing—we can't really regard these speculations as anything more than a lucky guess).

As the gel medium of the Liesegang process evidently makes diffusion a critical aspect, it's not hard to guess

from the preceding discussion that a reaction–diffusion process lies behind the pattern formation. But while this is no doubt the case, the phenomenon is not fully understood even today. One idea, which was first proposed by Ostwald a year after Liesegang published his findings, is based on the proposition that the reaction product does not precipitate until the solution becomes supersaturated above some critical threshold concentration. Precipitation can potentially occur as soon as the concentration of the reaction product becomes too high for the solution to bear—as soon as it becomes supersaturated. But in practice, particles of the insoluble product will grow large enough to precipitate only after they have first attained a certain critical size. This is one of the basic tenets of the theory of crystal growth, which Ostwald helped to establish. If the product molecules cannot cluster into these 'critical nuclei', the solution can become highly supersaturated.

Ostwald suggested that in Liesegang's experiments, formation of the critical nuclei was slowed down by the fact that the reaction product diffuses only slowly through the gel. The reaction is all the while increasing the degree of supersaturation, however, and once this exceeds a threshold, the concentration of the product is at last great enough everywhere for nucleation to occur. Then the nuclei grow rapidly, accreting the reaction product from the solution around it and precipitating as a dark band. Precipitation leaves the reaction front depleted in the product, and so precipitation stops—and it takes some time for it to build up again to the critical threshold, by which time the front has moved forward. This cycle of nucleation–precipitation–depletion dumps a train of bands in the wake of the front.

Ostwald's theory was refined in 1923 by K. Jabczynski, who showed that it could be used to predict the spacing between successive bands. Jabczynski's spacing law states that the ratio of the positions of two consecutive bands (defined relative to, say, the first band) approaches a constant value as the number of bands gets larger. The theory was further refined by Stephen Prager in 1956, who turned it into a well-defined mathematical model; but unfortunately Prager's model predicted that the bands will be infinitely narrow, which is certainly not what is observed. Peter Ortoleva at the University of Indiana and co-workers made further improvements to the theory in the 1980s to overcome this shortcoming. More recently, Bastien Chopard from the University of Geneva and colleagues have devised a cellular-automaton model which takes into account

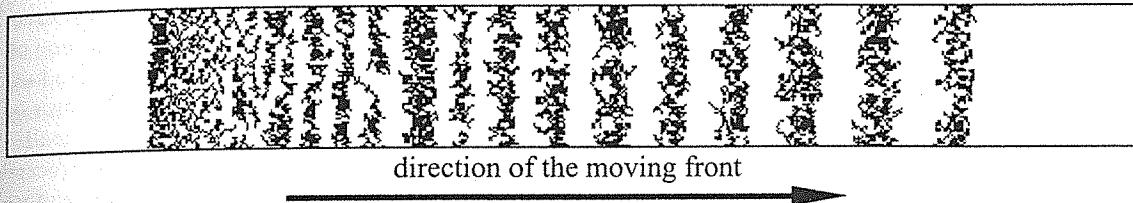
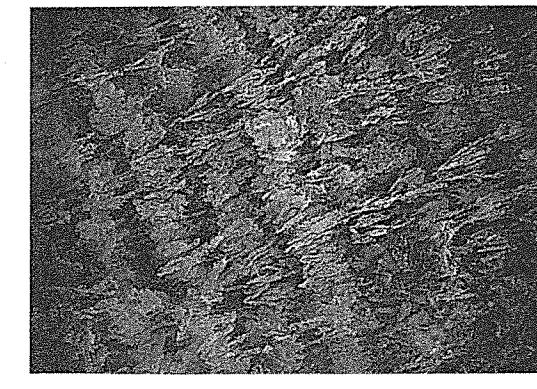


Fig. 3.13 Liesegang bands generated in a cellular automaton model of a precipitation-diffusion process. (Image: Bastien Chopard, University of Geneva.)

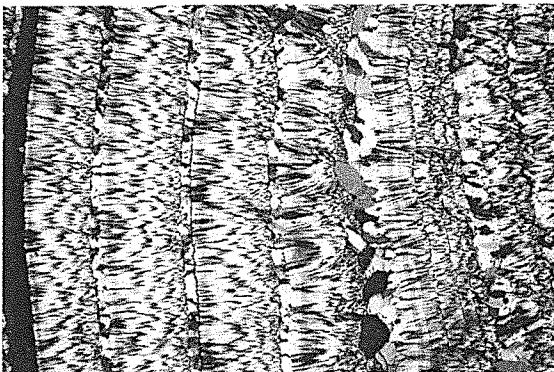
the microscopic processes that control the diffusion, nucleation and precipitation of the reacting species in Liesegang systems. Their model is able to produce precipitation bands (Fig. 3.13) which obey Jabłczynski's spacing law.

But the trouble is that the band spacings in real experiments don't by any means always observe this law: several different relationships have been reported, and there seems to be no general law that applies to all Liesegang-type experiments. Other explanations for the banding have been put forward, many of which generally involve processes that take place *after* nucleation has occurred. But with such a diversity of observations, it isn't hard to find results that will fit most models, while preventing unambiguous discrimination between them.

Liesegang realized that the banded patterns he saw were similar to those found in certain rocks. There is now good reason to suppose that many banded rock formations do indeed arise from cyclic precipitation as mineral-rich water infiltrates a porous rock and reacts to form an insoluble product. Amongst the mineral patterns that have been attributed to Liesegang-type processes are the bands seen in some iron oxide minerals, the wood-grain texture of cherts, the striations of a mineral called zebrastone, and perhaps most familiarly of all, the bands of agates. And Ostwald's idea is just one of a whole class of models involving particle transport, nucleation and precipitation that have been put forward to explain such formations. To take just one example: geologists Peter Heaney from Princeton University and Andrew Davis from the University of Chicago showed in 1995 that Liesegang precipitation-diffusion cycles can account for the iridescence of iris agates. Whereas the colour banding shown in Plate 6 is perhaps the most spectacular feature of these and other agates, the iridescence comes from a periodic banded structure on a scale too small to see by eye. The bands vary in width from about a tenth of a micrometre to several micrometres



a



b

Fig. 3.14 Liesegang banding at very small length scales in iris quartz gives it an iridescent appearance. (a) The bands here are about seven micrometres apart, and are caused by periodic differences in the concentration of defects in the crystal structure. (b) At a larger scale, thin bands of quartz alternate with thicker bands of chalcedony. The bands run from top to bottom; the horizontal striations have a different origin, caused by the fibrous structure of the mineral. The image here is about 2.5 mm across. Banding is also evident on scales of about a centimetre or so (Plate 6). (Photos: Peter Heaney, Princeton University.)



(Fig. 3.14a), and this banded 'grating' scatters visible light (because the light has wavelengths of comparable dimensions), creating the iridescent effect. Heaney and Davis showed that these bands correspond to differences in the crystal structure of the mineral: regions of highly crystalline quartz alternate with regions in which a high concentration of defects disrupt the regularity of the crystalline lattice. They postulated that the defective regions formed by the initial linking together of soluble silicate ions into long chains, which precipitate to give a poorly crystalline form of the mineral chalcedony. The highly crystalline regions, meanwhile, are formed by precipitation of individual silicate ions as quartz. This latter is possible when the concentration of silicate ions at the crystallization front is low. But because quartz precipitates slowly, silicate ions diffuse towards the front more rapidly than they are removed by precipitation, and eventually the concentration builds up to a degree that allows their linking into chains. Then the more rapid precipitation of chalcedony takes precedence, until this depletes the silicate solution once again.

Heaney and Davis pointed out that, while this mechanism could account for the iris banding, the agates are in fact patterned on several length scales. There are also oscillations between defect-rich chalcedony and defect-poor quartz with wavelengths of several hundred micrometres (Fig. 3.14b) and of a centimetre or so (Plate 6), suggesting that there are several *hierarchical* mechanisms for oscillatory patterning at play here. This kind of hierarchical repetition of pattern over several length scales is a feature of some of the patterns that we will encounter in later chapters.

Burn up

I have already mentioned that combustion processes are autocatalytic; but normally this doesn't produce anything more interesting than a big bang, because there is nothing to keep the process in check. When, however, an explosive combustion process such as the burning of hydrogen in air is conducted under experimentally well controlled conditions, oscillations in the reaction rate can arise. The overall reaction looks simple enough: two molecules of hydrogen combine with one of oxygen to form two molecules of water:



But the detailed evolution of this reaction is rather complicated, involving short-lived, reactive intermediate species such as lone hydrogen and oxygen

atoms and the hydroxyl free radical, OH. In an autocatalytic process, *three* molecules of hydrogen and one of oxygen can react with a lone hydrogen atom to produce two molecules of water and *three* hydrogen atoms—thus the products of this process represent a multiplication of the reactants. This autocatalytic process arises because hydrogen atoms are less reactive, and so hang around for longer, than oxygen or hydroxyl radicals. When the reaction of hydrogen and oxygen is carried out in a stream of flowing gases in a CSTR, the result of these autocatalytic processes is an oscillatory variation in the burning rate, which shows up as a rise and fall of the temperature generated in the combustion flame (Fig. 3.15). In effect, the mixture of gases repeatedly ignites and then subsides into an unreactive state. The reaction between carbon monoxide and oxygen—the same reaction as that studied by Ertl's group, but this time carried out by burning the free gases rather than bringing them together on a catalytic metal surface—also shows oscillatory behaviour in a CSTR.

Can these combustion processes also generate spatial patterns if they are not well mixed? Well, it has been known for a long time that when a hydrocarbon fuel such as butane is burnt in a flame under carefully controlled conditions, the flame can become very non-uniform, separating into a number of distinct cells. The cells are bright regions, separated by darker boundaries where the temperature is lower and there is less emission of light by the excited gas molecules. These cellular flames were first reported by A. Smithells and H. Ingel in 1892, who described a flame that separated into petal-like segments that rotated around the flame's axis. George Markstein made a careful study of such flames in the 1950s, and in 1977 G.I. Sivashinsky showed theoretically that the cell patterns could be the result of

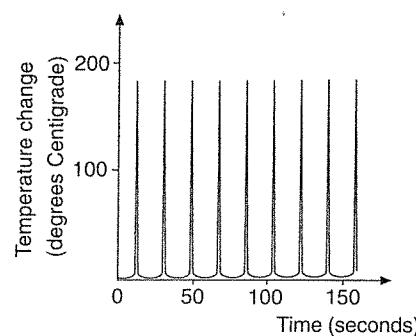


Fig. 3.15 Oscillations in the combustion of hydrogen in a flow reactor, revealed by variations in the temperature. (After: Scott 1992.)

a reaction–diffusion process. A burning flame requires both fuel (generally a hydrocarbon like butane) and oxygen—the former cannot burn without the latter. But molecules of these two compounds travel (diffuse)

through the gas mixture at different rates—the oxygen molecules are lighter and so diffuse more rapidly. The combustion reaction can be sustained only as long as the rates of diffusion of both species are sufficient to

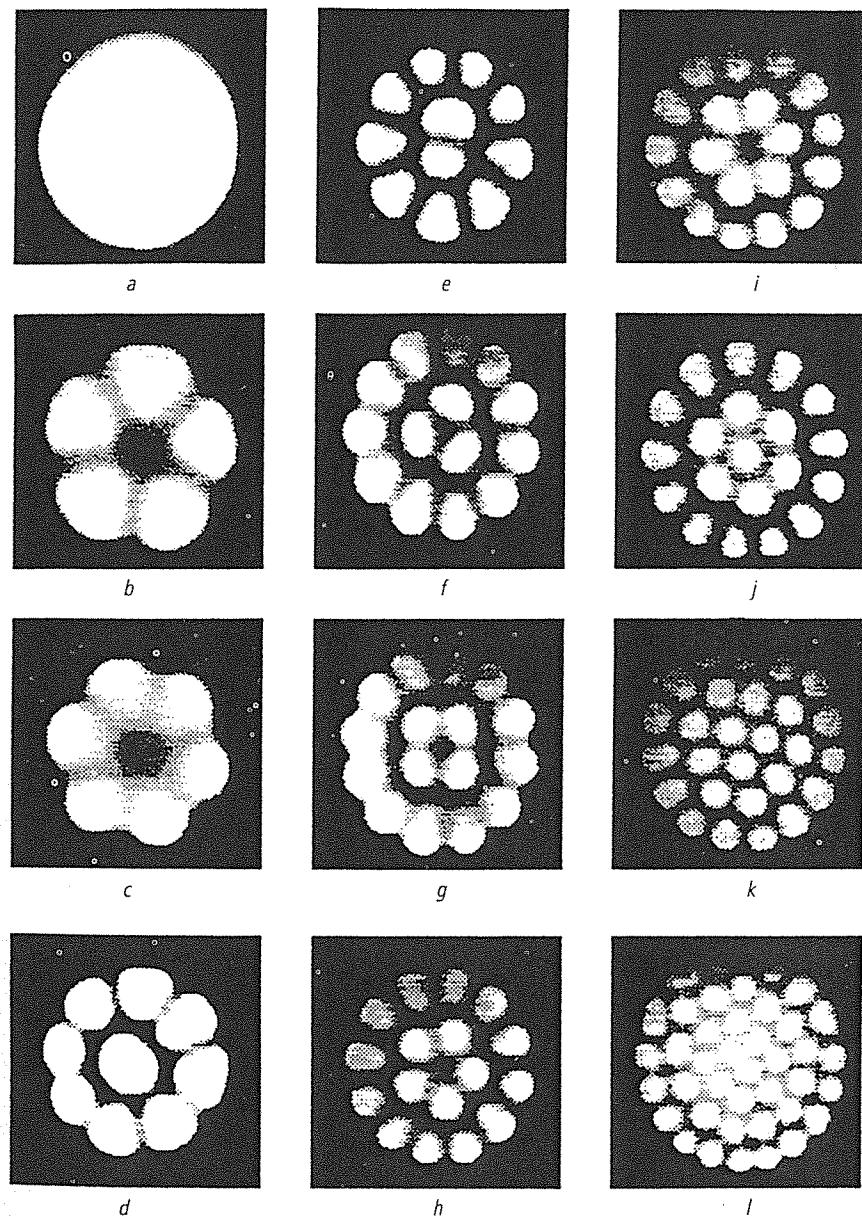


Fig. 3.16 Cellular patterns in a shallow cylindrical flame seen from above. The temperature of the flame is lower in the dark regions. (These dark regions are not truly dark to the eye; they are simply a result of the limited dynamic range of the video tape on which the images were recorded.) The cellular flames adopt ordered states. Here I show a sequence of ordered states of increasing complexity as the rate of gas flow in the flame is increased. (Photos: Michael Gorman, University of Houston, Texas.)



Reaction-diffusion process

feed it. Spatial irregularities can arise when the oxygen in one region burns up the fuel more rapidly than it is replenished by diffusion, and combustion cannot then continue until more fuel diffuses there. Another theory was developed around much the same time, however, which held that flow effects in the gas streams, not molecular diffusion, were responsible for cellular flames.

Sivashinsky showed that the diffusive mechanism could in principle produce ordered hexagonal arrangements of cells. But the cells that Markstein and others had reported were irregularly shaped and were in constant, disordered motion, breaking up and coalescing. It was not until 1994 that Michael Gorman and Mohamed El-Hamdi of the University of Houston in Texas and Kay Robbins of the University of Texas at San Antonio found the first clear examples of regular patterns in cellular flames.

They studied flames of a butane–oxygen mixture passing through a stainless steel plug in a cylindrical chamber. The flame appeared as a luminous disk just half a millimetre thick. As the researchers increased the rate of gas flow through the disk, they saw an initially uniform disk-shaped flame break up into a ring of cells (Fig. 3.16). When the cells first appeared, there were four of them; but as the flow rate was increased, a fifth and then a sixth cell appeared. Increasing the rate still further created a new inner ring of cells, which multiplied from one to six and then spawned a third ring (Fig. 3.16*j*). An hexagonal array of cells appeared as the last ordered structure; for higher flow rates the cells began to exhibit rapid, chaotic motion in which no recognizable pattern was apparent.

The overall number of cells in each concentric ring stays steady for a given flow rate, but their positions keep altering. In some experiments, each ring of cells seemed to rotate independently in a kind of hopping motion: the cells would stay put for a while, then the whole ring would abruptly rotate like a gear wheel shifting position. Under other conditions the motion was more chaotic: the ordered states might disappear intermittently into randomly shaped cells, and then reappear (Fig. 3.17). Sometimes the innermost cells took on a spiral shape, which circulated like a rotating yin-yang symbol.

The Texas researchers concluded that Sivashinsky's diffusion mechanism, not gas-flow effects, lies behind the ordered patterns that they saw—mainly because the latter mechanism was expected to produce bigger cells than those observed. These ordered cellular flames rep-

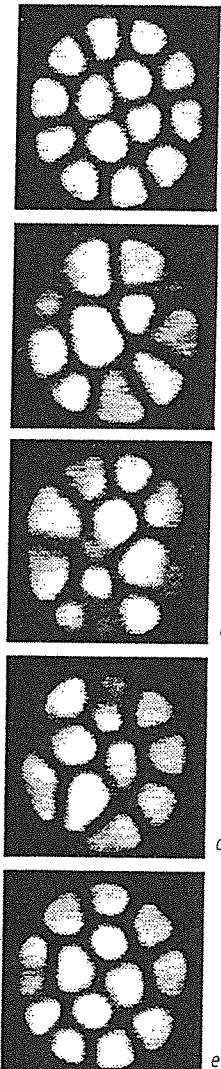


Fig. 3.17 Under some conditions, ordering in the cellular flames is intermittent, being interrupted sporadically by the appearance of more-random cell arrangements. Time advances here from (a) to (e). (Photos: Michael Gorman.)

resent an unusual kind of dynamic reaction–diffusion pattern, however, because they are all unstable, undergoing intermittent rearrangements via more chaotic states. On the other hand, Howard Pearlman of NASA's Lewis Research Center and Paul Ronney of the University of Southern California have observed flame patterns that look very much like the spiral waves of the BZ reaction, reinforcing the idea that they are the products of a reaction–diffusion process.

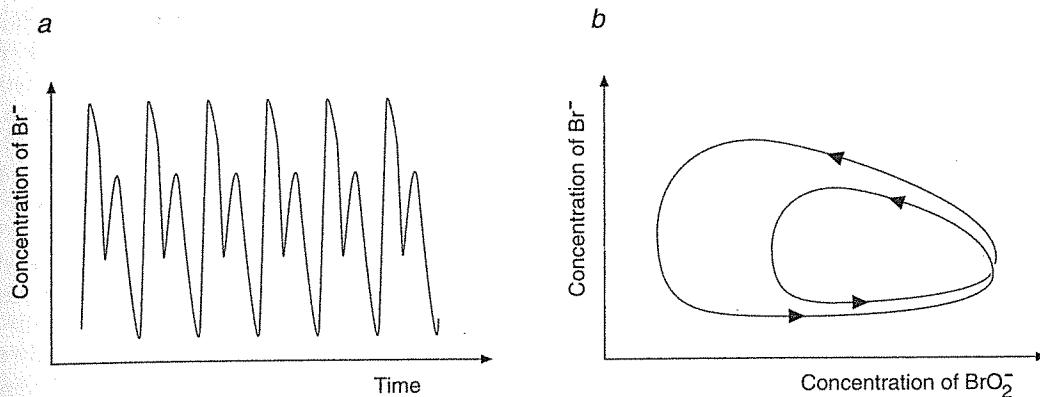


Fig. 3.18 As the flow rate of a BZ mixture in a continuous stirred-tank reactor is increased, the oscillations double up, a phenomenon called periodic doubling (a). The limit cycle of the period-doubled oscillations develops two loops (b).

Going wild

Another thing that this combustion process and the BZ reaction share in common is that gradual changes in the flow rate of the reacting molecules do not induce correspondingly gradual changes in behaviour; rather, there are abrupt jumps to a new mode of behaviour when a certain threshold is reached. In the well-mixed BZ reaction conducted in a CSTR, I indicated that the oscillatory behaviour defines a certain limit cycle that remained robust in the face of changes in, say, flow rate or initial concentrations of the reagents. But this is true only up to a point. If the flow rate is increased far enough, the colour-changing mixture suddenly starts to exhibit a new temporal pattern. It alternates between blue and red, sure enough, but if we were to time the colour changes—or better still, to measure the rise and fall in concentration of one of the intermediates such as the bromide ion—we would find that something new has happened. The switching now appears to have a double pulse (Fig. 3.18a). Plotted as a limit cycle, this behaviour manifests itself as a double loop (Fig. 3.18b). The system has to traverse both lobes before it repeats itself.

This is called a period-doubling bifurcation, and it was observed in the BZ reaction in the 1980s by J.C. Roux and co-workers. ‘Period-doubling’ is obvious enough—the system now has two stable pulses or periods. ‘Bifurcation’ simply means that the stable, oscillating state of the system has forked into two, with each state corresponding to a loop of the limit cycle.

I should point out that the initial oscillatory state of the BZ mixture in a CSTR is itself the product of a bifurcation, because the flow rate has to reach a certain threshold before the indefinitely oscillating colour change is stable at all; below this flow rate, the reaction will simply go through a series of transient colour changes before settling down into an unchanging, uniform state. (Admittedly, this may take some time, which is why ‘clock’ reactions like this still look temporarily like regular oscillators even in a closed vessel.) This kind of abrupt transition from a stable, steady state to an oscillatory one was first identified mathematically by the German Eberhard Hopf, long before anyone knew about chemical oscillators. It is therefore called a Hopf bifurcation. Hopf bifurcations are a common source of periodic motion from initially steady motion—the mathematicians Ian Stewart and Martin Golubitsky describe them appealingly as the onset of a wobble.

It does not yet seem to be clear whether the transitions seen in cellular flames are indeed Hopf bifurcations or some other kind of bifurcation. All the same, both these and the period-doubling jumps seen in the BZ mixture in a CSTR share the characteristic that they just keep on coming as the flow rate is increased, giving patterns of ever more complexity. In the latter case, a further increase in flow rate induces another bifurcation into a limit cycle with four lobes, and then eight, and so forth. In cellular flames, each jump adds more cells or even a new ring of cells. With each jump, the amount that the flow rate has to be *further* increased to induce another bifurcation decreases: the jumps get closer and closer together and the patterns become more and more

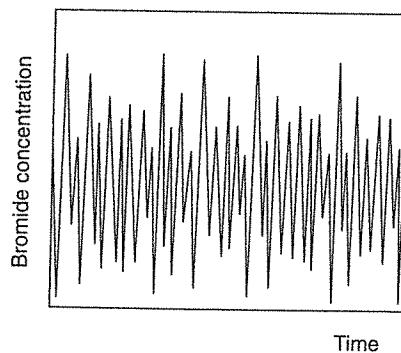


Fig. 3.19 At high flow rates, the oscillations of the BZ reaction become apparently random—the system becomes chaotic.

complex (which is to say, of lower and lower symmetry). There eventually comes a point at which all pretence of pattern is thrown to the winds and the system descends into chaos. For the BZ reactor, this means that the oscillations in concentrations no longer show any sign of periodicity at all—they appear to be random (Fig. 3.19). The cellular flames, on the other hand, dissolve into a random pattern of irregular cells that is forever shifting.

The route to chaotic behaviour through a series of period-doubling bifurcations is a common one, seen in

many diverse systems that exhibit chaos, including lasers and populations of predators and their prey (Chapter 9). Very clear period-doubling bifurcations leading to chaotic oscillations have been seen in the combustion of carbon monoxide and oxygen gases in a CSTR (Fig. 3.20). There are other ways for a chemical system to become chaotic too, and Jack Hudson and colleagues at the University of Virginia identified one such in the late 1970s. In studies of the BZ reaction in a CSTR at high flow rates, they saw ‘mixed-mode’ oscillations in which a single cycle involves both small- and large-amplitude oscillations (Fig. 3.21a). Typically, each large-amplitude oscillation (in the concentration of, say, bromide) is accompanied by a little train of small oscillations—perhaps just one, perhaps more. Under some conditions these mixed sequences keep repeating regularly, but in other cases different mixed modes may alternate with no apparent periodicity (Fig. 3.21b). Although these non-periodic states satisfy all of the mathematical criteria for chaos (which distinguish them from purely random processes), there was much debate initially about whether they were genuine examples of ‘chemical chaos’ rather than effects induced by poor mixing in the experiments. But it is now clear that theoretical models of oscillatory reactions (which don’t have to suffer any experimental deficiencies) can gener-

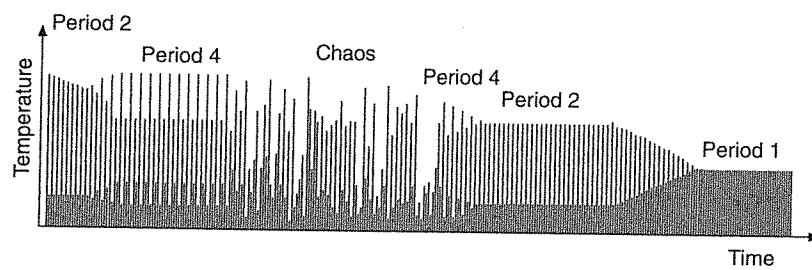


Fig. 3.20 Period doubling and the transition to chaos in the reaction of carbon monoxide and oxygen in a flow reactor. (After: Scott 1992.)

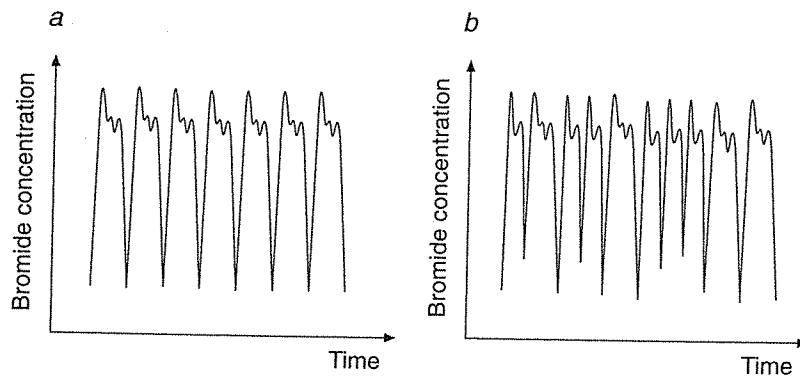


Fig. 3.21 Mixed-mode oscillations in the BZ reaction consist of a mixture of large- and small-amplitude oscillations (a). Mixed modes may alternate apparently at random (chaotically) when the flow rate is high (b).



ate chaotic mixed modes, so this seems to be a *bona fide* example of a new route to chaos.

Rhythms of life

Chemical waves are not merely a curiosity conjured up in laboratories under highly specialized conditions. For many living organisms, ourselves included, they are a matter of life and death.

Heart attacks are the leading cause of death in industrialized nations. The majority of these result from a pathological condition of the heart called ventricular fibrillation—a medical term which, roughly translated, means that the heart forgets how to beat. Instead of acting in a coordinated manner to generate a regular pumping motion, the tissues of a heart that has entered into ventricular fibrillation lose their ability to execute large-scale coordinated contractions, and the heart appears to flutter feebly to no great effect, like a frightened bird. During the onset of ventricular fibrillation, the heart enters a kind of behaviour called cardiac arrhythmia, which, despite the name, actually denotes a new rhythmic activity in which the regular beats of about one per second give way to rapid pulsations about five times faster. These eventually dissolve into uncoordinated fibrillation, leading to sudden cardiac death. That eventual heart stoppage in such cases is preceded by this frenzied activity was recognized as early as 1888, when J.A. MacWilliam described the fateful events in colourful terms: 'The cardiac pump is thrown out of gear, and the last of its vital energy is dissipated in a violent and prolonged turmoil of fruitless activity in the ventricular wall'. These changes in heart activity can be seen in electrocardiograms, which record the change in electrical voltage in a region of the heart tissue (Fig. 3.22).

How do cells in a healthy heart act in synchrony in the first place? Each heartbeat corresponds to a travelling wave of electrical activity, which begins at a pacemaker region of the heart called the sinoatrial node and travels throughout the heart tissue. At the front of this travelling wave, the electrical voltage across the cell walls alters as electrically charged ions move from one side to the other. The wave of electrical activity (which is akin to a nerve impulse) induces muscle contraction, causing the heart to pump blood. Once the wavefront has passed, the cells become refractory (immune to a further pulse of electrical activity), while they 'reset' their across-membrane voltages by redistributing the ions. Thus, heart tissue is an excitable medium, and the heartbeat is induced by a spatio-temporal pattern—a travelling wave—very much akin to that of the BZ reaction. This is one of the major reasons why the BZ reaction has attracted such interest: scientists are interested in the patterns not only for their own sake (pretty as they are) but because they might provide us with a model to help understand some aspects of heart behaviour.

It now seems clear that the fatal condition of ventricular fibrillation is associated with the initiation of spiral waves in the heart. You can see from Plate 5 that spiral travelling waves in an excitable medium tend to have a shorter periodicity than target waves (adjacent wavefronts are closer together). The consequence of this is that, once they are created, spiral waves come to dominate over target waves, because they 'jump in' to excite the medium more quickly. A clue to the role of spiral waves in ventricular fibrillation (VF) is given by the fact that, when cardiac arrhythmia is initiated, the frequency of the heart's oscillations increases.

It is now possible to see these lethal spiral waves directly in beating hearts. Early experiments involved

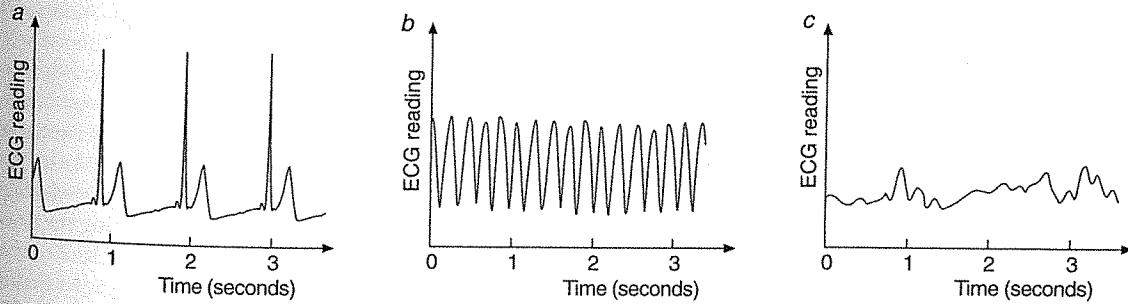


Fig. 3.22 The onset of ventricular fibrillation is evident in electrocardiograms as a transition from regular heartbeats a few seconds apart (a), to rapid oscillations that flutter several times a second (b), a condition called cardiac arrhythmia. Finally this regular behaviour dissolves into the feeble, uncoordinated behaviour of ventricular fibrillation (c), which is quickly fatal if not arrested.



studies of fragments of heart tissue, kept 'active' by mimicking physiological conditions: suspending the tissue in a salt solution and supplying nutrients (glucose) and oxygen. In such an experiment, researchers from the University of Amsterdam were able in 1972 to see evidence of a wave of electrical activity spinning like a turbine blade, at ten revolutions per second, in a piece of rabbit heart tissue. Subsequent studies showed these pirouettes ever more clearly, but it was not until 1995 that they were revealed in whole hearts. Richard Gray and co-workers at the Health Science Center of the State University of New York showed that a single rotating spiral wave could give rise to VF in whole rabbit and sheep hearts sustained in a culture medium. They followed the patterns of electrical activity propagating through the hearts by adding to the artificial 'blood' supply a dye that emitted fluorescent light whose brightness was a measure of the local voltage. The researchers saw spiral waves of electrical activity whose centres meandered over the surface of the heart (Fig. 3.23a). The electrocardiograms associated with this behaviour showed the uncoordinated oscillations characteristic of VF (Fig. 3.23b).

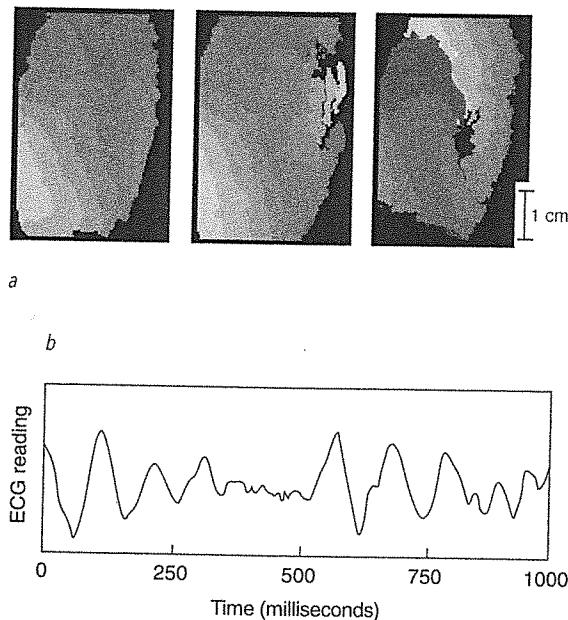


Fig. 3.23 A spiral wave developing in a rabbit heart, traced out by monitoring voltage-dependent dyes (a), and the associated electrocardiogram trace (b). (Image: Richard Gray, State University of New York Health Science Centre.)

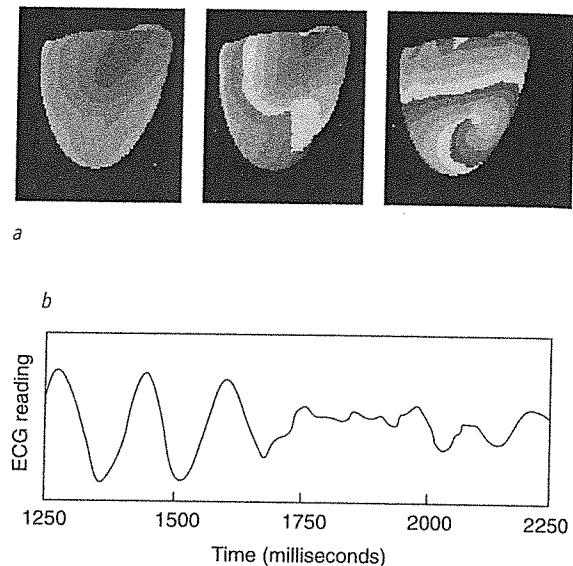


Fig. 3.24 A spiral wave in a numerical model of the heart (a), and the associated electrocardiogram trace (b). (Image: Richard Gray.)

The rotating spiral waves in these experiments are not easy to see in the spatial maps of electrical activity, at least without a trained eye. But Gray and his colleague José Jalife carried out simulations of the heart behaviour on a computer, using equations that were known to describe the basic properties of heart activity. In their simulations, the spirals were very clear (Fig. 3.24a and Plate 7), and when the model was adjusted to allow the tips of these waves to meander, the simulated electrocardiograms were very similar to those seen in the real sheep hearts (Fig. 3.24b).

How might spiral waves arise out of the regular travelling waves found in healthy hearts? It seems likely that obstacles of 'inert' tissue, such as damaged tissue caused by blood clots, can act as the initiating points for such waves. Travelling wavefronts have to pass around such obstacles, which are immune to excitation themselves, and this can make a steadily propagating wave begin to rotate. Just this kind of behaviour has been seen in the BZ reaction when some obstacle like a physical barrier is placed in the way of a target wave (Fig. 3.25). In the heart, small areas of damaged tissue don't obviously present much of a threat in terms of impeding the flow of blood or the regular contraction of the rest of the heart. But this research on travelling waves shows that if they trip up the heart's spatio-temporal patterns, the result can be a switch from health to a life-threatening condition.

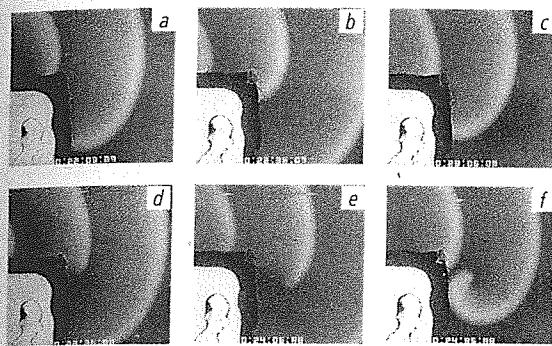


Fig. 3.25 The initiation of a spiral wave when a travelling wave in the BZ reaction encounters a barrier. (Photo: James Keener, University of Utah; from Agladze *et al.* (1994). *Science* **264**, 1746.)

Microbial crosstalk

The cells in any organ need to stay in touch and act in a coherent way, and in both the heart and the brain these interactions can result in regular oscillations and spatio-temporal patterns that are an important characteristic of the organ's healthy functioning. But of course some cells get by just fine on their own—bacteria, which are single-celled, are beyond doubt the most successful organisms on the planet. If we pride ourselves in surviving under conditions ranging from the burning Gobi desert to the frozen Arctic tundra, we should recapture some humility by observing that bacteria are to be found also in hot oil hundreds of feet below the ground, in superheated water around miniature submarine volcanoes, and amidst toxic radioactive waste.

But even for organisms as adaptable and resilient as bacteria, it sometimes pays to cooperate. For even bacteria need the basics—food, water, warmth. When these things become scarce, some bacteria adopt a remarkable survival strategy, in which we can see nature's own version of the BZ pattern-forming system. If times are tough—if food becomes scarce, say—evolution has taught the bacteria that they are then better off foraging in groups. So it becomes necessary for each bacterium to tell the others—who are blind, deaf and dumb—where it is.

Bacteria have evolved a clever way of doing this: they perfume themselves. The cells emit a chemical compound, called a chemoattractant, into the medium around them, much as animals emit pheromones to attract mates. Other bacteria can sense how much of this chemical signal is coming their way from different directions, and they start to move in the direction where

the concentration of the chemical rises most rapidly—in other words, they wriggle along the steepest gradient in chemoattractant concentration. This chemically stimulated movement is called chemotaxis.

Chemotaxis is not unique to bacteria, but is employed by other single-celled organisms too, and is also utilized by our own body cells to form complex structures such as neural dendritic cells in the brain. It is a versatile mechanism for pattern formation, and nowhere is

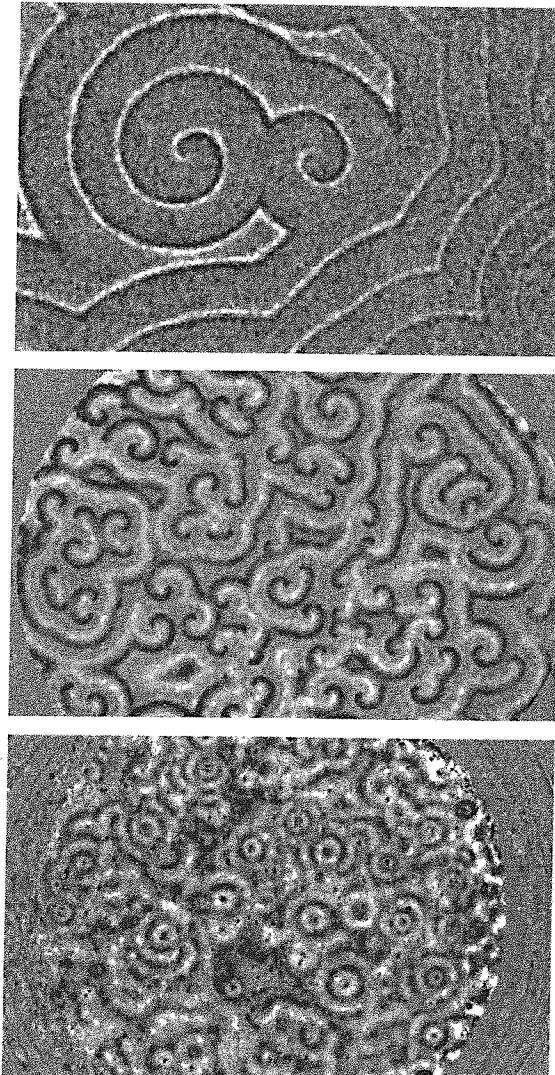


Fig. 3.26 Target and spiral patterns in colonies of the slime mold *Dictyostelium discoideum*. These patterns are generated when some cells emit periodic pulses of a chemical attractant, towards which other cells travel. (Photo: Cornelis Weijer, University of Dundee.)



this better illustrated than in colonies of the slime mold *Dictyostelium discoideum*. These single-celled organisms start up their chemical cross-talk when deprived of heat or moisture, and this communication allows them to aggregate into multicellular bodies that are more fit to survive hardship. Certain cells, called pioneer cells, release pulses of the compound cyclic adenosine monophosphate (cAMP), and nearby cells then follow this chemical trail to its source. Once a cell has emitted a burst of the chemoattractant, it falls silent for several minutes, as if recuperating from the exertion. This refractory period means that, when a slime mold colony starts to undergo chemotaxis, it behaves as an excitable medium. We saw earlier that the target and spiral waves of the BZ reaction turn out to be the *generic* patterns of excitable media, and so it may come as no surprise that the slime mold shows these patterns too (Fig. 3.26).

But the patterns are just a passing phase. Ultimately they fragment into distinct, branched islands of cells. The spirals and targets are simply a way of getting the

self-organization and aggregation underway. Eventually the cells converge into isolated clumps, which thenceforth act cooperatively. Yet that is by no means the end of the story: the clumps pile up into mounds which can be regarded as individual multicellular organisms. Cells in different parts of the mound 'differentiate', which means that they are no longer equivalent but act out different roles. Each mound develops a bulbous body—the 'fruiting body'—perched on a long stalk. The fruiting body contains many spores, which can survive without food or water until such time as these become available again.

The initial stages of this aggregation process, involving travelling waves, can be modelled on the basis of precisely the same principles as the BZ reaction. The 'pacemaker' of the chemical waves is a biochemical reaction through which the signalling molecule cAMP is manufactured by the pioneer cells. cAMP is made from a molecule called adenosine triphosphate (ATP) in a reaction catalysed by an enzyme called adenylyl cyclase, which is attached to the inside of the cell mem-

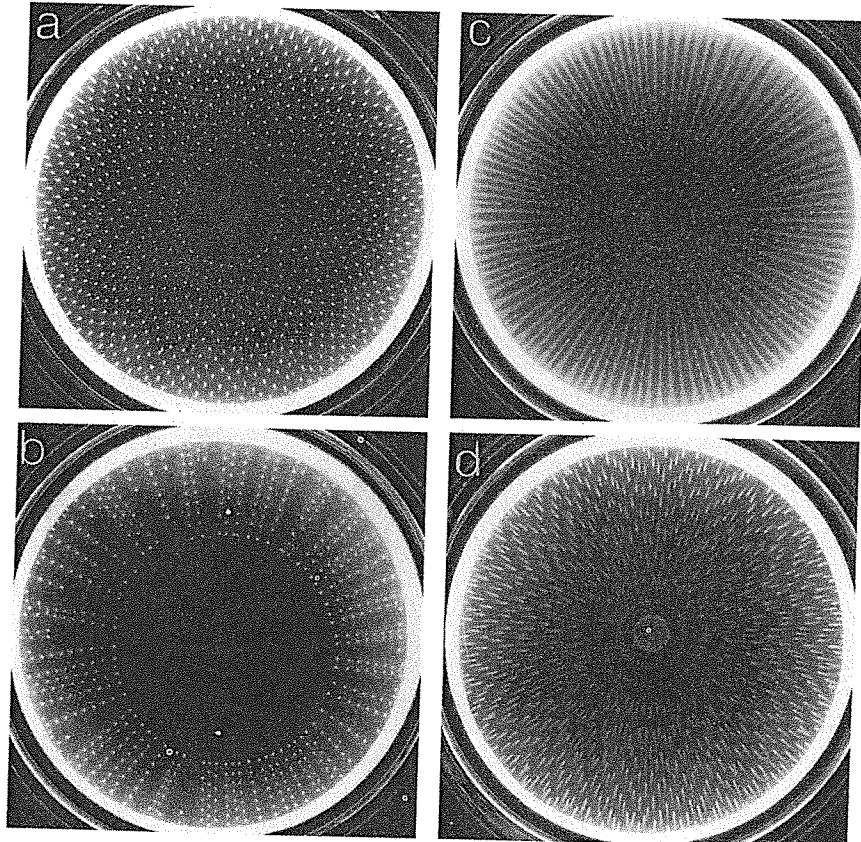


Fig. 3.27 Symmetrical patterns formed by the bacteria *Escherichia coli* in response to chemical signals. (Photos: Elena Budrene, Harvard University.)



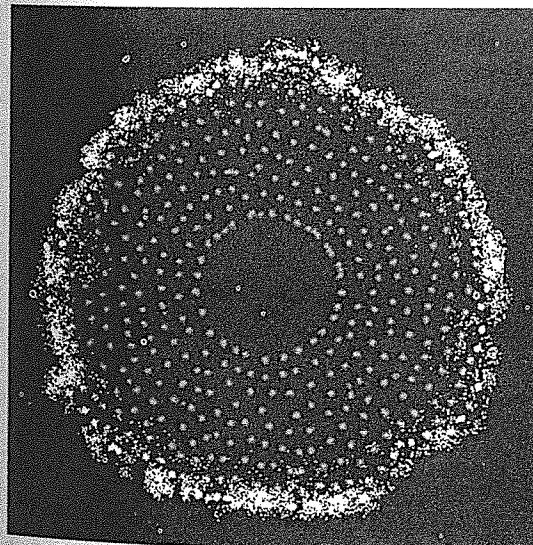
brane. The cAMP diffuses out of the cell through the membrane. There it can continue to diffuse into the surrounding medium and excite nearby cells; but alternatively it can become involved in a feedback loop that regulates the formation of more cAMP. In the latter case, cAMP outside the cell interacts with another protein molecule in the cell membrane in such a way that the protein is stimulated into influencing the catalytic activity of the adenylate cyclase enzyme. In this way, cAMP produced by the enzyme can enhance the rate at which further cAMP is formed. This autocatalytic behaviour can give rise to bursts of cAMP production followed by quiescent periods.

Bacterial black holes

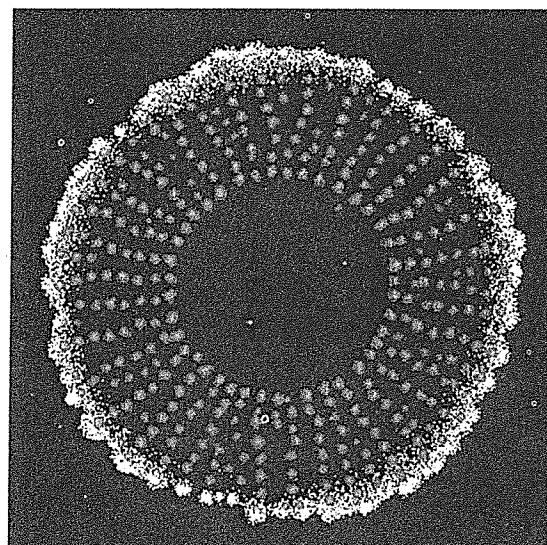
In 1991 Elena Budrene and Howard Berg of Harvard University expanded the repertoire of patterns that chemotaxis was known to generate. They reported astonishing patterns that developed in colonies of *Escherichia coli*, bacteria that live in the human gut, when the colonies grew in a semi-solid agar gel under life-threatening conditions—lack of food, too great an oxygen concentration, the presence of molecules that disrupt protein manufacture in the cells, or even just coldness (Fig. 3.27). Unlike the travelling waves of *Dictyostelium*, these patterns remain stable for long

periods. Budrene and Berg realized at once that the patterns were the result of chemotactic signalling between the bacteria, which emit a chemoattractant called aspartate under stress. But their sheer complexity and variety—much richer than the familiar targets and spirals of *Dictyostelium*—baffled everyone.

Nonetheless, it seemed likely that the patterns were again the result of a competition between a handful of basic processes: cell multiplication by division, cell migration (diffusion) in search of food, and cell clustering by chemotaxis once the local density of cells (and thus the local rate of chemoattractant formation) exceeds a certain threshold. Eshel Ben-Jacob and colleagues from Tel Aviv University in Israel attempted to reproduce the spot patterns in a cellular automaton model that captures these basic features of the bacteria's behaviour. I will describe this model in more detail in Chapter 5, where I show that it can mimic many of the branching patterns formed by growing bacterial colonies. In essence, the model postulates groups of bacterial cells that move *en masse*, consuming food, reproducing and emitting a chemoattractant if food becomes scarce. The model generates an expanding ring of cells, which cluster into spots behind the advancing front when they attract one another through chemotactic signalling (Fig. 3.28a). The spot patterns become



a



b

Fig. 3.28 Concentric spots (a) and radial patterns (b) of clustering bacteria can be reproduced in a cellular automaton model in which groups of cells migrate, reproduce, and respond to attractive and repulsive chemical signals from one another. (Images: Eshel Ben-Jacob, Tel Aviv University.)

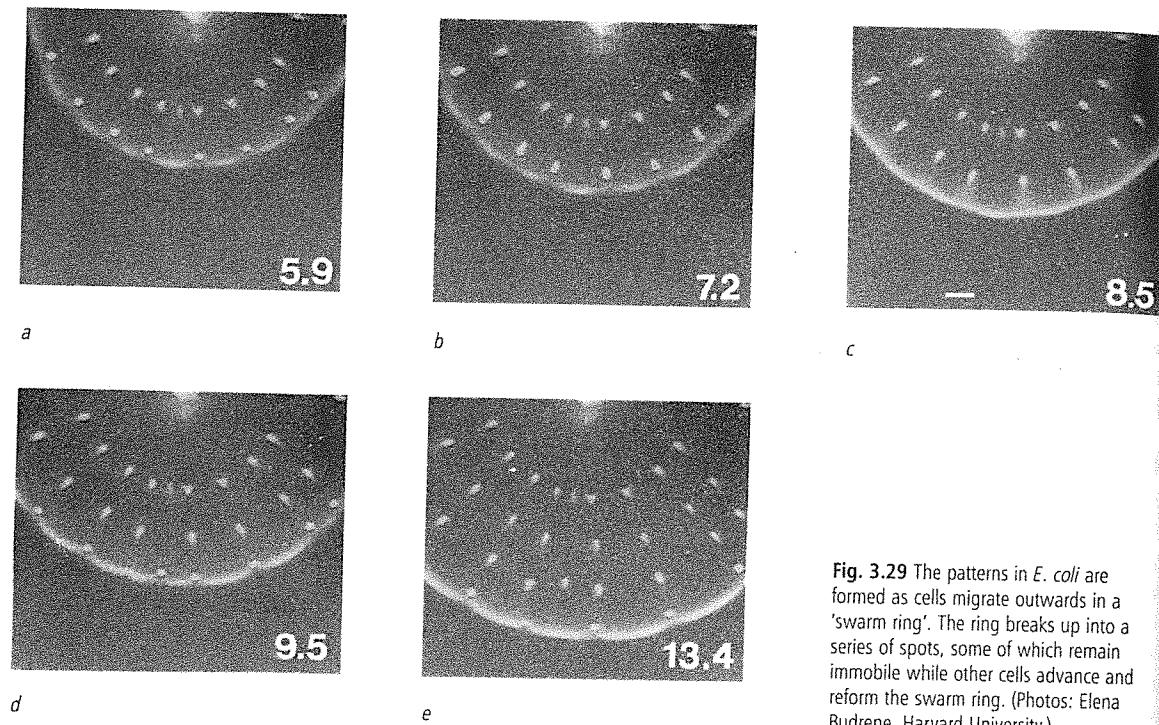


Fig. 3.29 The patterns in *E. coli* are formed as cells migrate outwards in a 'swarm ring'. The ring breaks up into a series of spots, some of which remain immobile while other cells advance and reform the swarm ring. (Photos: Elena Budrene, Harvard University.)

aligned along radial lines, as in the experiments, if a further component is added to the model: a repulsive interaction between the bacterial clusters, resulting from their emission of a chemical signal that warns other clusters to stay away. Radial spots then emerge from a delicate balance between attractive and repulsive interactions (Fig. 3.28b). Whether real *E. coli* bacteria exude a chemorepellent of this sort is, however, an open question. At the same time, Herbert Levine and Lev Tsimring at the University of California at San Diego proposed an alternative model that included the same kinds of interactions but described the bacteria's motions using reaction-diffusion equations akin to those first studied by Ronald Fisher in the 1930s, instead of invoking discrete cellular automata. This model also generates rings that break up into clusters behind the advancing front of the colony.

Budrene and Berg were meanwhile taking a closer look at what each clump of cells gets up to. In 1995 they reported that the symmetric patterns are the result of a very complex process in which the cells alternate between forging out into new territory and stopping to cluster into groups. The whole process, watched in time-lapse video, resembles a peculiar cycle of boldness and indecision.

First the bacteria disport themselves in a ring, which moves outwards from the central source (Fig. 3.29). Budrene and Berg call this a swarm ring, and it takes about a day to expand to the edges of a Petri dish. In order to produce the chemoattractant (aspartate), the cells need to be provided with the compound succinate in the culture medium—they carry out enzymatic chemical transformations which turn succinate into aspartate. If the amount of succinate is very low, there is little chemotaxis and the ring simply expands uniformly. But at higher concentrations of succinate, the swarm ring collapses suddenly (within a few minutes) into a series of more or less equally spaced clusters of cells around its perimeter, as if the advancing party of bacteria has paused and formed into little groups to discuss their next move. This instability of the swarm ring happens when the cells, which are excreting aspartate as they advance, have finally made enough of this attractant to trigger its spontaneous break-up into clusters, a process that breaks the circular symmetry.

Once one cluster forms, the parts of the ring to either side become unstable and clustering propagates in a kind of 'domino effect' all around the ring. But some cells are not drawn into these clusters, and they head out again in the swarm ring, multiplying as they go. As this



cycle repeats, a trail of clusters in radial lines is created behind the advancing ring (Fig. 3.29e).

Although this sequence of events is not unlike that seen in the models of Ben-Jacob, Levine and their colleagues, Elena Budrene was not convinced that either represents a 'minimal model' whose ingredients are nothing more than the known biological properties of the bacteria. With colleagues Michael Brenner and Leonid Levitov from the Massachusetts Institute of Technology, she has developed a different model which suggests that patterning can result from the interplay of the following processes:

1. Diffusion and multiplication of the bacteria.
2. Production of the aspartate chemoattractant.
3. Diffusion of aspartate.
4. Consumption of succinate to make aspartate.
5. Chemotactic drift of cells towards regions of high aspartate concentration.

The researchers used Fisher-type reaction-diffusion equations to describe each of these processes. They showed that the expansion of the swarm ring is driven by the consumption of succinate: the cells move progressively outwards as they deplete all the succinate in the medium behind the ring. This drive to find fresh succinate even outweighs the lure of the chemoattractant, which serves simply to ensure that the ring remains a well defined circular band instead of getting smeared out by diffusion of the cells.

The instability leading to break-up of the ring into clusters, meanwhile, emerges from the model as a consequence of 'singular' solutions of the equations. These arise from a positive feedback process: above a certain threshold density of cells, they collectively produce so much attractant that any slight irregularity in density is rapidly amplified until the cell population becomes focused into a sharply defined, very dense point. That this instability might occur in chemotactic populations was first suggested in 1973, and it was later dubbed 'chemotactic collapse'. It can be loosely compared to the formation of an astrophysical black hole: as the density increases, so it encourages the accretion of even more mass, until the density at the central point blows up and, in the equations, becomes infinite. Of course, the cell density in these bacterial black holes cannot *really* become infinite; ultimately it is halted by the depletion of some essential substance such as oxygen in the 'singularity'.

So Budrene, Brenner and Levitov proposed that chemotactic collapse leads to the break-up of the swarm

rings into a series of spots. They suggested several reasons why their model might provide a more realistic description of the process than the earlier ones. For one thing, it accounts for the marked difference in observed timescales for swarm-ring expansion and break-up. And it doesn't require any biochemical processes other than those already known. Furthermore, the formation of the patterns does not require fine-tuning of the model parameters—the clustering instability is a general and robust property of the equations, because the singular solutions are catastrophic and so pretty insensitive to the fine details.

One of the difficulties of modelling these bacterial tapestries is that they are so diverse. The bacterium *Salmonella typhimurium* has its own palette of patterns, including spots, concentric rings and spotty rings, while *E. coli* also displays amazing chevron structures (Plate 8). We will see still more, very different, patterns in Chapter 5. James Murray and Rebecca Tyson of the University of Washington, along with S.R. Lubkin of North Carolina State University, have proposed a model that purports to capture all of the pattern-forming mechanisms, and many of the patterns, seen in *E. coli* and *S. typhimurium*, while remaining faithful to the known biology. Their model is again based on reaction-diffusion, incorporates equations describing the diffusion and uptake of the nutrient (succinate) and chemoattractant (aspartate) and the migration and proliferation of cells. The researchers suggest that their model does more than just generate patterns similar to those observed in the experiments (you can make a reaction-diffusion model do just about anything, as we'll see in the next chapter)—it reproduces some of the features of the way the patterns appear, a hopeful indication that the visual coincidences are down to more than fortuity. But while the details will continue to be debated, it seems highly likely that a reaction-diffusion mechanism of some kind is capable of accounting for these bacterial kaleidoscopes.

In the beginning

Chemical waves may be with us from birth. Certainly that is the case if one is a frog: following fertilization, pulses of calcium ions are released over the surface of the egg. The reason for these calcium waves isn't entirely clear, but they are probably a kind of chemical signal that, like a radio wave, carries information through space encoded in its amplitude and frequency. In 1991 David Clapham from the Mayo Foundation in Rochester, New York, and colleagues observed spiral

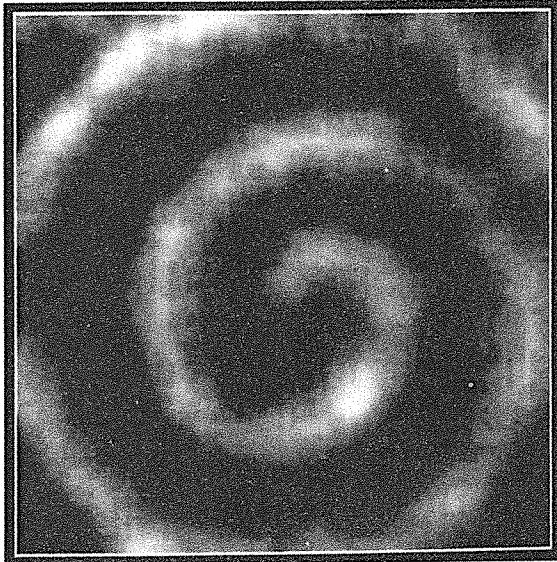


Fig. 3.30 Spiral waves of calcium travel across the surface of frog eggs when they are fertilized. The purpose of these waves in embryo development is as yet unclear. (Photo: David Clapham, Mayo Foundation, Rochester.)

waves propagating and annihilating on the surface of fertilized frog eggs (Fig. 3.30). These eggs behave as an excitable medium, like the heart, or like the plain old Belousov–Zhabotinsky brew.

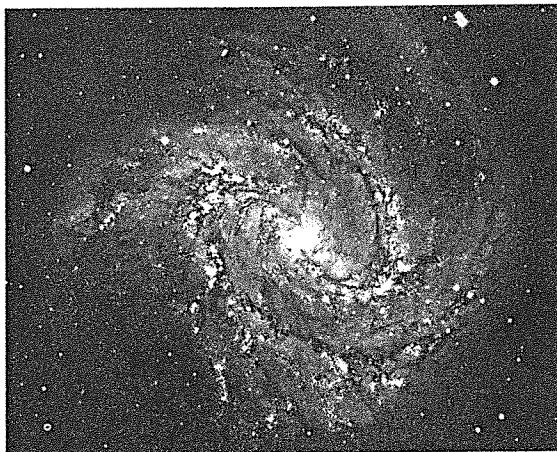


Fig. 3.31 The spiral galaxy NGC 5236 in the southern sky. The structure of some spiral galaxies may result from a star-formation process with the characteristics of a reaction–diffusion system. (Photo: European Southern Observatory.)

At the other end of the scale, astronomer Lee Smolin at Pennsylvania State University has suggested that the formation of some spiral galaxies (Fig. 3.31) can be regarded as a kind of reaction–diffusion process. These cosmic spirals are so familiar to us now that it is worth remembering that not all galaxies are spirals: some are smooth elliptical blobs, some are lens-like disks (lenticular) and others have irregular shapes that defy easy categorization. But it is clear that galaxies have a strong tendency to form rotating spirals (our own Milky Way galaxy is of this type), and Edwin Hubble proposed in the 1920s that this is the pattern towards which more featureless elliptical galaxies evolve, via lenticular forms.

Galaxy structure has been studied for a long time, but there is still much to debate. In the late 1920s Bertil Lindblad suggested that the spiral structure was a natural consequence of the interplay between rotation and the gravitational interactions of the stars, but it wasn't until the 1960s that C.C. Lin and Frank Shu showed how a spiral galaxy formed in this way could avoid being pulled apart by centrifugal forces as it rotates. They proposed that the spiral arms are not rigid (stars are not either in them or out of them) but are waves of enhanced stellar density that sweep through the rotating disk.

Smolin points out that there are some spiral galaxies in which this idea of a density wave doesn't hold up: the spirals are instead tracing out regions of enhanced star formation. Why should stars form in one place in the galactic disk but not in another? Smolin proposes that the rate of star formation is influenced by positive and negative feedbacks. The positive feedback (auto-catalysis) comes from dust produced in the atmospheres of stars that have formed already, which helps the clouds of interstellar particles to condense into new stars. Negative feedback comes largely from the ultraviolet light emitted by existing stars, which heats up the interstellar medium and makes it less likely to condense. In addition, Smolin argues that certain aspects of the star-formation process give it characteristics akin to a diffusion process. The galaxy then becomes a reaction–diffusion system, with all the pattern-forming potential that entails—making it permissible to view these cosmic pinwheels as gargantuan relatives of the whorls on a frog's egg.

Yes, say hello to life's universal patterns. We'll be seeing more of them.