Chapter 5.

Nonlinear dynamics: complexity, phase transitions, criticality, bifurcations and pattern formation.

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5.1. Introduction.

Hydrothermal mineralising systems are archetypal, large, nonlinear, evolving systems in which a number of interacting parts and processes result in highly irregular spatial and temporal distributions of alteration mineral assemblages, of deformation such as fracturing, veins and breccias, at a number of scales, and of mineralisation and sulphides. The evolution of these systems involves a number of phase transitions such as unaltered → altered, undeformed → brecciated, and un-mineralised → mineralised. These features are some of the hallmarks of systems that are now widely studied under the umbrella of *Nonlinear Dynamical Systems*, a subject that has evolved significantly over the last 120 years since the pioneering works of Poincaré (1892), Gibbs (1902; *Dover rendition*, 1960), Lotka (1910, 1920), Onsager (1944), Prigogine (1955), Lorenz (1973) and Mandelbrot (1974). The literature associated with Nonlinear Dynamical Systems is now too large to adequately review or summarise here and much new material is emerging each month particularly in the fields of non-equilibrium critical systems and pattern formation in very large non-equilibrium systems.

The purpose of this chapter is to provide an introduction to those parts of the subject relevant to pattern formation in nonlinear systems that undergo phase transitions far from equilibrium. The intent is to introduce the concepts and terminology that enable the reader to delve deeper into the literature and to appreciate the tools that are required to study hydrothermal mineralised systems as nonlinear dynamical systems. We try to keep the discussion non-mathematical but some mathematics (which one can skip at a first reading) is required to develop a feel for the subject. We try to explain the mathematics in words. The tools themselves are the subject of Chapter 9.

In order to understand hydrothermal systems one needs to appreciate the various forms that natural systems can take and how hydrothermal systems fit into the various classifications of systems that exist. Clearly a hydrothermal system with its irregular distributions of alteration mineral assemblages, brecciation, overprinting parageneses, veining and mineralisation is a complicated system but is it complicated in the sense that network configurations in the global internet system or in the human brain form complicated systems? Are there lessons we can learn from other complicated systems such as the World Wide Web or biological systems that we can apply to help us understand hydrothermal systems? There are a number of questions we seek answers for to shed some light on these issues in this chapter: Hronsky (2011) and McCuaig and Hronsky (2014) refer to hydrothermal systems as *self-organised, critical systems*. *What does this mean*? *What is a critical system*? *Is there more than one form of critical system*? *If so, are hydrothermal systems special critical systems in some manner*? *Are hydrothermal systems, in fact, critical*? *What makes a system self-organise*? *How can we test if a hydrothermal system is self-organised or critical? What features of the irregularity in hydrothermal systems can we measure that are of use in helping us to understand the irregularity*? *What tools are useful in helping us to quantify the irregularity*? *How do we use* *such quantification to test models of ore formation and distribution? And, above all, how can we use the irregularity in an exploration sense?*

To place the present chapter in context and give some motivation we present in Figure 5.1 some data sets from hydrothermal systems. Figures 5.1 (a and b) show abundances of chlorite and gold measured along diamond drill-holes in ore mineralised systems in the Yilgarn of Western Australia. The chlorite data set resembles at least superficially the plots for deterministic systems shown in Figures 1.13. The gold data resemble more an intermittent signal that one might see in a turbulent fluid (Frisch, 1995) or the energy release in an earthquake sequence (inset Figure 5.1 b). The questions we ask here are: *Do these signals represent the response of a critical system? Are the signals fractal or even multifractal? Or are they something else? Is there some kind of systematic behaviour in these signals that reflects the nonlinear dynamics of the system?*

In Figures 5.1 (c and d) we show behaviour at larger scales where the fractal dimension of regional scale "complexity" has been mapped in Figure 5.1 (c) and correlated with gold occurrence whilst in Figure 5.1 (d) the distribution of fractures at the hand specimen scale is shown in a breccia from the Tropicana deposit in Western Australia. Again we ask similar questions: *Do these represent critical systems? Are they multifractal in nature? Can we discern something about the nonlinear dynamics of the system from these data sets?*

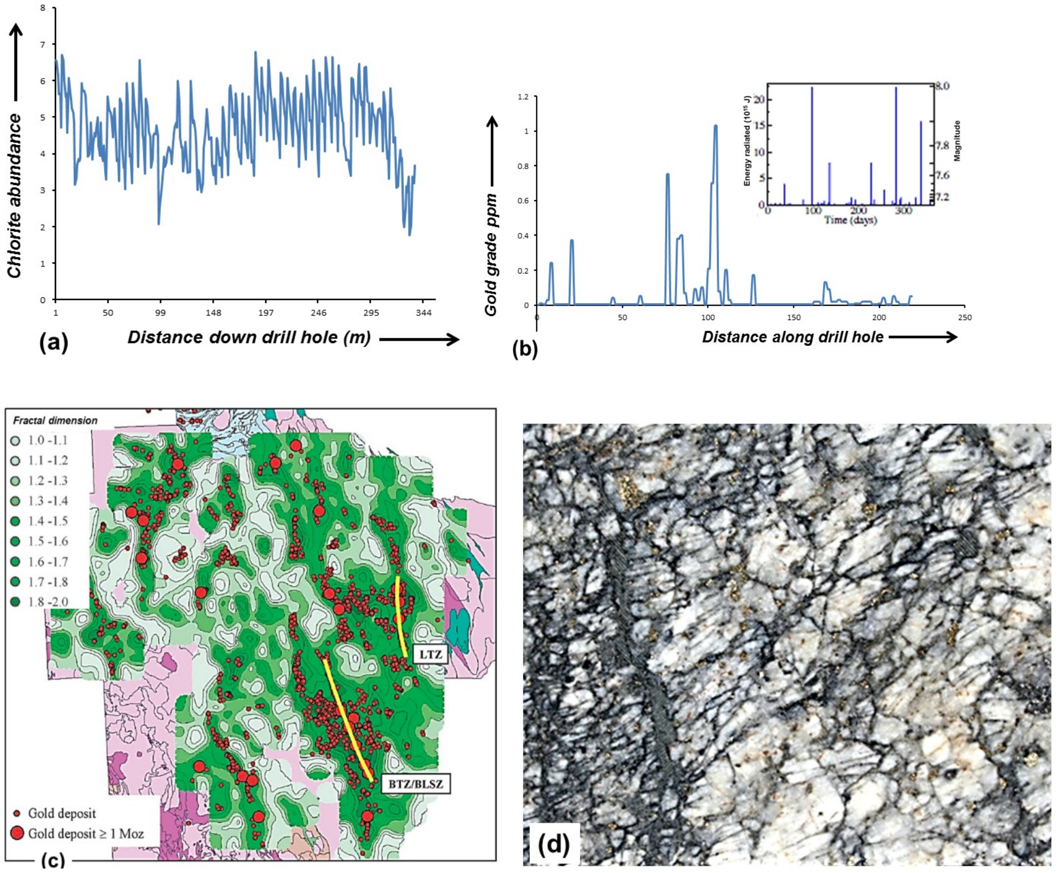

Figure 5.1. Data sets from hydrothermal systems. (a) Chlorite abundance along a drill hole measured by infra-red reflectance methods. Salt Creek gold deposit, Western Australia. (b) Gold abundance along a drill hole measured by

assay. Salt Creek gold deposit, Western Australia. Inset: energy release sequence for earthquakes in California, 1995. (c) Map of "complexity" in part of the Yilgarn of Western Australia. The figure is a contoured map of fractal dimension (determined by box counting) of mapped structures with gold occurrences superimposed. Yellow lines show locations of the Bardoc Tectonic Zone and Boulder – Lefroy Shear Zone (BTZ/BLSZ) in the Kalgoorlie Terrane and the Laverton Tectonic Zone (LTZ). After Hodkiewicz et al. (2005). See that paper for details. (d) Image of fractures in a breccia from the Tropicana gold deposit in Western Australia. Scale: Image is 1.5 cm across base.

In this chapter we first consider how hydrothermal systems fit into the general discipline known as *Nonlinear Dynamical Systems* and then explore the differences between *complicated* and *complex* systems; complex systems are those where a number of nonlinear interacting processes influence each other at a number of scales so that the overall behaviour is the result of these interactions rather than the behaviour being the collective outcome of a number of non-interacting processes. Complex systems do not need to be complicated and not all complicated systems are complex. We then proceed to discuss the general concept of a *phase transition*. We distinguish two types of equilibrium phase transitions: *first order (or abrupt)* and *second order (or continuous) phase transitions* the first of which is *not critical* whereas the second is *critical*. However it is now recognised that there exist a large number of non-equilibrium phase transitions, some of which are critical and others non-critical. We spend some effort in discussing the characteristics of *critical phase transitions* and comparing them with structures that arise through a *bifurcation*.

A characteristic of complex systems as opposed to complicated systems is the phenomenon of *emergence* whereby ordered or structured patterns can spontaneously arise from an otherwise homogeneous system. *Emergence* is discussed in terms of *self-organised* and *pattern forming* processes. In any complex system, processes operate at a number of different scales and so the resulting patterns depend in their spatial distributions on length scales in different manners. This results in structure development at all spatial scales and structures at different scales that may show long range correlations or anti-correlations or no correlation what so ever for a particular scale. Such distributions are called *fractal distributions*. Commonly fractals of different scaling and correlation behaviours are embedded in each other; the resulting distributions are called *multifractal distributions*. We use these concepts in this chapter but defer a detailed discussion to Chapter 6.

To guide the discussion we first list the important patterns that need to be considered for mineralised (and un-mineralised) hydrothermal systems:

- At the global scale there seems to be both a secular and a spatial ordering of mineralised sites.
- At the regional scale there is a power law distribution of ore body size and grade together with a strong correlation of mineralised sites with complexity in the underlying infrastructure.
- At the regional scale there appears (based on two studies, one in Zambezi and the other in Nevada) to be what has been called a bifractal spatial distribution of mineralisation. This means the spatial distribution follows one fractal distribution at coarse spatial scales and another fractal distribution at finer scales (see Figure 12.2b).
- At the local scale fracture systems are multifractal in geometry.
- At the mineralised scale multifractal distributions of ore grade and alteration appear to be well documented.
- At the ore body scale zoning of alteration and mineralisation is sometimes well developed.

Comment [A1]: This is the final synthesis chapter - which has just been changed to Chapter 13.

- At the grain-scale apparently irregular microstructures develop that for the most part do not resemble those seen in many metamorphic rocks. Grain shapes are irregular and compositional heterogeneity exists at all spatial scales.

  We discuss these various issues throughout this chapter.

5.2 Nonlinear Dynamical Systems.

The classical linear approach to the behaviour of systems is that they are either *deterministic* or *stochastic*. The term *deterministic* is meant to imply that if one knows the initial conditions of the system and the ways in which the boundary conditions have changed with time then the behaviour of the system at some future time can be predicted. *Stochastic* implies that processes operating during the evolution of the system interact in a random manner so that the final outcome of the interactions can only be predicted in terms of probabilities.

The fundamental question that needs to be answered in gaining an understanding of hydrothermal mineralising systems is:

If the behaviour of hydrothermal systems is governed by a series of deterministic equations (those that describe deformation, chemical reactions and heat and fluid flow), why are such systems characterised by apparently stochastic spatial distributions of deformation, alteration and mineralisation?

Poincaré (1892) was the first to show that even a small number of interacting nonlinear processes (in his case, three) can result in irregular behaviour but his work was not widely embraced until perhaps the 1970's when it became accepted that for nonlinear systems (even very simple ones) irregular behaviour is the norm rather than an interesting exception. We, in the geosciences community, still need to make that transition, both in understanding and acceptance, with respect to most processes that take place in the lithosphere of the Earth.

We have seen in Chapter 1 that even system behaviour described by the simple relation (the so-called *logistic equation*):

$$x_{N+1} = \alpha x_N \left(1 - x_N\right) \qquad (5.1)$$

can result in an irregular response. Moreover, the long term behaviour, given some initial value of *x*, can be calculated but not predicted by analytical means. The behaviour appears stochastic but is in fact deterministic.

However a serious limitation on long term prediction for such a system in a real life situation is the extreme sensitivity to initial conditions displayed by this system so that two almost identical systems with almost imperceptible differences in initial conditions will ultimately diverge exponentially[1] in behaviour. Thus although the behaviours of two almost identical systems are completely deterministic the final difference between the two systems is only predictable if we know the tiny differences in initial conditions; such knowledge is generally not available and so in this sense the behaviour is unpredictable. Such sensitivity to initial conditions is known as *chaos*.

Since the behaviour of such nonlinear systems is unpredictable from a pragmatic point of view, the evolutionary trajectory of the system can only be described in terms of probabilities; in other

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[1] The exponent that describes this exponential divergence (or convergence in some cases) is known as the *Lyapunov exponent*, λ. In a time series, if two signals begin with a separation, ΔS_0, then the separation, ΔS, after time *t* is: $\Delta S = \exp[\lambda t]\Delta S_0$. If λ is positive the two signals diverge. If λ is negative they converge. λ is a measure of the predictability of a system.

words, the behaviour appears to be stochastic. It is convenient in such systems to describe the behaviour in terms of *phase space* which is simply a space with coordinate axes that define the various states of the system during its evolution.

The simplest of such phase spaces is the P-T phase diagram that is used to describe the various states (mineral phases) that exist at chemical equilibrium for various initial chemical compositions. For a mechanical system not at equilibrium the commonly used coordinate axes are the spatial positions and velocities of particles making up the system. For a non-deforming chemical system not at equilibrium, a convenient phase space could have as coordinates the concentration (or activity) of each mineral phase together with the temperature and pressure.

The probability distributions that describe system evolution in phase space universally have three characteristics:

(i) In general the trajectories tend to concentrate in certain parts of the phase space called an *attractor*. The attractor commonly has structure within structure and so is a fractal. Such fractal attractors are called *strange attractors*.

(ii) Some parts of the attractor are visited more often than others so that the probabilities in commonly visited or rarely visited regions of the attractor may diverge exponentially from those in the remainder of the attractor or there may arise discontinuities in the probability distributions across the attractor. These regions are called *singularities*[2] in the probability distribution and the attractor then becomes multifractal with a spectrum of measures of singularity strength.

(iii) The sensitivity to initial conditions means that the effects of such uncertainty may grow faster in some parts of the attractor than in others. This also contributes to the multifractal nature of many attractors.

As an example of such an attractor we present Figure 5.2 (b) for the generalised Hénon map (Sprott, 2003, pp 129 – 131) given by the iterative equations:

$$x_{\mathrm{N}+1} = a_1 + a_2 x_{\mathrm{N}} + a_3 y_{\mathrm{N}} + a_4 x_{\mathrm{N}}^2 + a_5 x_{\mathrm{N}} y_{\mathrm{N}} + a_6 y_{\mathrm{N}}^2$$
$$y_{\mathrm{N}+1} = x_{\mathrm{N}} \qquad (5.2)$$

where we have selected $a_1 = -0.7$, $a_2 = 0.3$, $a_3 = -0.7$, $a_4 = 1.8$, $a_5 = -0.7$ and $a_6 = 1.4$ with initial values of x and y given by $x_0 = y_0 = 0.05$. These equations represent a system more general than the logistic equation (5.1); in (5.2) two components, x and y, interact with each other in a nonlinear manner and the value of one depends on the value of the other and itself in a previous iteration. This type of behaviour is similar to networked chemical reactions where the evolution of two chemical reactions depends on the supply of products from each other in order to continue the reactions (Chapter 8). Here we consider each iteration to be a step in time, t. The plot (which we remind the reader is deterministic) of $y_{\mathrm{N}+1}$ against time is given in Figure 5.2 (a) and the attractor, which is in the phase space with coordinates x_{N} and y_{N} is given in Figure 5.2 (b). Attractors for other values of a_1 through to a_6 are given in Sprott (2003, p 130).

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[2] Mathematically, a singularity is some behaviour of a function that cannot be defined mathematically. This may mean, for instance, that the function is discontinuous, diverges to infinity or that it is not differentiable at a particular point.

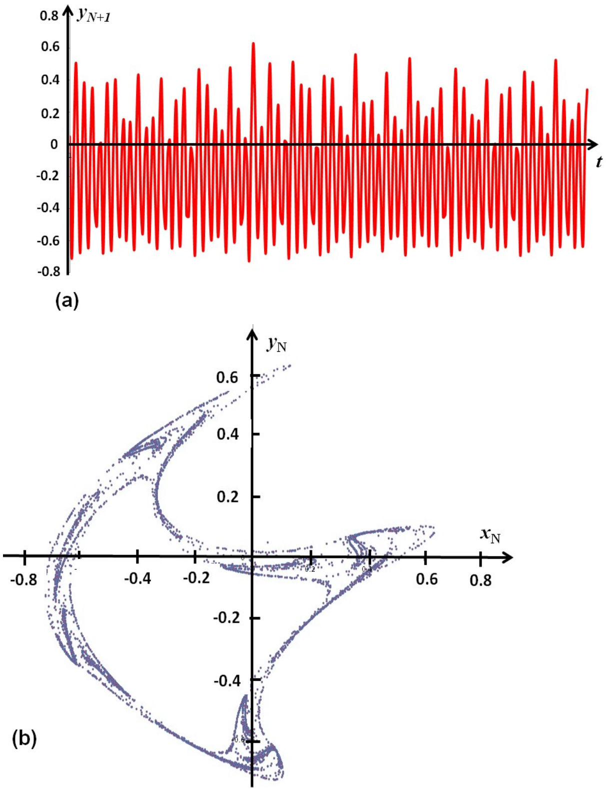

Figure 5.2. Results from the generalised Hénon map given by (5.2) and values of a_1 to a_6 given in the text. (a) Plot of y_{N+1} for the first 250 iterations. (b) The attractor for (5.2) for the first 1000 iterations. To see this attractor for the first 2.5 x10^5 iterations and several others for (5.2) with different values of the parameters a_1 to a_6 refer to Sprott (2003, his figure 6.1). Notice that some parts of the attractor are visited more often than others. These regions are singularities in the attractor. The reader can readily reproduce these figures and explore results for other values of a_1 to a_6 (such as are presented by Sprott) using an EXCEL spreadsheet.

The discipline now called *Nonlinear Dynamical Systems* has developed to encompass a toolbox that enables us to understand, quantify and describe the behaviour of both deterministic and stochastic chaos and it is the purpose of this chapter to discuss some aspects of such systems. The elements of the toolbox are left to Chapter 9.

The subject has developed along the same lines as that of classical *Statistical Mechanics* applied to large systems and so includes the Thermodynamics of Chaotic Systems (Beck and Schlögl, 1993). In the subject called *Classical Thermodynamics* the quantities of interest, namely, temperature, pressure, chemical potential and entropy arise as averages of effects resulting from the interactions of a large number of particles (atoms). In the *Thermodynamics of Chaotic Systems* a large number of particles or interactions between particles may not exist and the quantities involved arise from the interactions of the large number of *states* in phase space inherent in chaotic systems. The thermodynamic state quantities involved: pressure, temperature, chemical potentials and entropy, have the same names as in Classical Thermodynamics and arise from the same averaging and limiting procedures as in

Classical Thermodynamics although they may not have the same physical significance attributed to these quantities as in Classical Thermodynamics. In addition thermodynamic state variables such as the Gibbs and Helmholtz energies (Beck and Schlögl, 1993, Chapter 6) and the specific heat can also be defined for chaotic systems (Beck and Schlögl, 1993, Section 12.4). We briefly expand on the correspondence between classical Statistical Mechanics and the Thermodynamics of Chaotic Systems in Chapter 9. For clarity we refer to state variables such as energy, temperature, pressure and so on defined for chaotic systems as the *statistical energy*, *statistical temperature* and so on to distinguish these from the same state variables derived and used in classical statistical mechanics and thermodynamics. We emphasise that conceptually there is no difference in the two approaches.

In addition, other quantities become of interest namely the *fractal dimension* of the system and other measures called *generalised fractal dimensions* (also known as *Rényi Dimensions*) that are of use in describing *multifractals*. We expand on these concepts in Chapter **9.**

In particular, nonlinear dynamical systems can undergo *phase transitions* where the qualitative behaviour of the system changes under the influence of one or more *control parameters*. One form of these transitions for equilibrium systems is called an *abrupt transition* where some measure of the energy of the system is continuous at the phase transition (Figure 5.3 e) but the first derivative of that function is discontinuous in exactly the same way that the temperature derivative of the chemical potential (the entropy) is discontinuous at a classical first order phase transition in a chemical system (Figure 5.3 g).; such transitions are not associated with a *critical point*.

A second form[3] of phase transition is a *continuous transition* where an energy function is continuous at the transition (Figure 5.3 f) but the *second* derivative of that function is discontinuous (Figure 5.3 j). An example is where the temperature derivative of the chemical potential (the entropy) is continuous at the phase transition (Figure 5.3 h) but the first derivative of the entropy (the specific heat) is discontinuous (Figure 5.3 j). These transitions are characterised by a *critical point* that marks the phase transition. A fundamental question is: *Does the transition from an un-mineralised to a mineralised system constitute a phase transition*? *And if so, is the transition marked by a critical point*? For proponents of the concept of self-organised criticality applied to mineralised systems the answer is clearly yes. But we need tools to test quantitatively such an hypothesis.

The principles behind the tools are discussed in Chapter 6 and the tools in Chapter 9. An excellent modern text on Statistical Mechanics and phase transitions is Sethna (2006). For a thorough and definitive discussion of the thermodynamics of chaotic systems see Beck and Schlögl (1993). For a detailed discussion of nonlinear dynamical systems in general see Wiggins (2005) and for a discussion of nonlinear behaviour, including chaotic behaviour, in chemical systems see Epstein and Pojman (1998). Criticality (including self-organised criticality) is

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[3] These forms of phase transitions are classically referred to as second order transitions (Atkins, 1978) but the usage is misleading since the important feature that characterises these types of transitions is that the specific heat (and other quantities that characterise the system) scales with distance from the transition temperature, T_t, in Figure 5.3 (right hand column). We use the terms *abrupt* and *continuous* transitions where others might use the terms first and second order transitions.

discussed in some detail in Sornette (2008). For a discussion of methods and tools used to analyse chaotic systems see Sprott (2008).

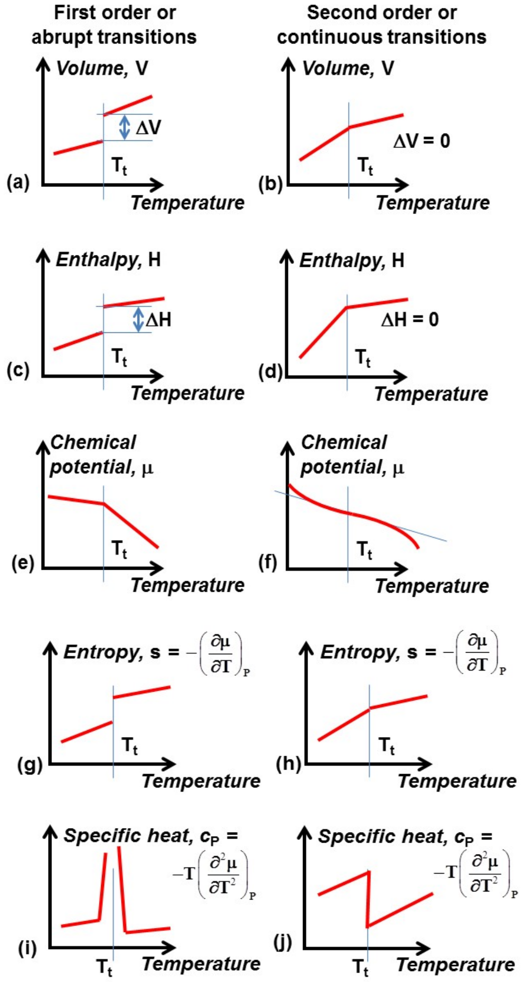

Figure 5.3. The classical view of the distinguishing features of first, or abrupt, (left hand column) and continuous (right hand column) equilibrium phase transitions for a pure material. (Modified after Atkins, 1978 and Sethna, 2006). T_t is the transition temperaure. In classical equilibrium thermodynamics T_t is not a critical temperature for abrupt transitions but is a critical temperature for continuous transitions.

5.3 Complicated and complex systems.

A distinction needs to be made between *complicated* and *complex* systems. Complex systems are characterised by emergent behaviour whereby spontaneous patterns or order appear from a homogeneous or disordered system as the outcome of the interactions of several collective, coupled processes. These processes involve repetitive, nonlinear interactions that influence each other at a number of scales. Each individual process may have a small probability of occurring and may have negligible feedback interaction upon itself. The overall evolution of the system results from the cumulative interactions of these processes and can result in organised behaviour known as *emergence* during which spatial and/or temporal patterns develop from a previous disordered system. This emergence does not involve a nucleation stage followed by a growth stage but rather involves a global response that derives from repetitive, competitive interactions. Some people use the term *self-organisation* to mean *emergence* but as indicated elsewhere in this book we prefer terms such as emergence or pattern formation since they have no anthropomorphic connotation.

The classical reductionist approach of dismantling a system and analysing the function of each constituent part tells us little about the way in which a complex system works or evolves in space or time. One needs to understand the interactions and feedback processes operating instead. Emergence is the result of the interacting dynamics within the system. Thus the precipitation of gold and its irregular distribution in a hydrothermal system cannot be understood by only defining the chemical reactions involved. Such an understanding can only be arrived at through an analysis of the interacting chemical, hydrological, thermal and mechanical dynamics of the whole system (see Chapter 8).

An example of a complicated but non-complex system is a highly sophisticated, mechanical wrist watch. One can understand how the watch works by dismantling it and describing the interactions between all the gears, levers and springs. The operation of the watch can be predicted precisely once these interactions are understood. The output of the device is strictly periodic behaviour that is quite insensitive to local fluctuations in temperature, gravity and other environmental factors.

Complex systems come in many forms, the most famous of which is represented by the family of *reaction-diffusion equations* (Murray, 1993; Epstein and Pojman, 1998) where diffusion of chemical species (which tends to homogenise the system) competes with the nonlinear production of chemical species by coupled chemical reactions (that tend to localise the system). We look at these types of processes in Chapter 8. For the moment we take another system called the *directed flow (or bond) percolation model* (Hinrichsen, 2005) since it is relatively simple and illustrates a number of concepts that we will use later on. The model is presented in Figure 5.4 and can be thought of as a fluid flow system in a lattice where the flow along the lattice bonds is governed by probability rules but is directed as if driven by a pressure gradient.

For this particular version of the directed bond model we select a square lattice (Figure 5.4 a) with a single seed at the vertex of the array. If one considers this as a flow system then we propose that the connections between nodes in the lattice can open or close with a probability, p. The result of open flow paths (marked in red) for one such probability is given in Figure 5.4 (a) together with a table on the right that records the number of active nodes, $N(t)$, at each time instant, t. This system undergoes a quantitative change in behaviour, or a *phase change*, at a critical probability, p_c, (Figure 5.4 b). At criticality, $(p = p_c)$, and after criticality, $(p > p_c)$, structure appears in the distribution of active bonds and the total behaviour of the system can be described in terms of three quantities: (i) the density, ρ, of active nodes that survive in the process, (ii) the spatial correlation length[4], $\xi_{\perp}$, (figure 5.4 c), (iii) the temporal correlation

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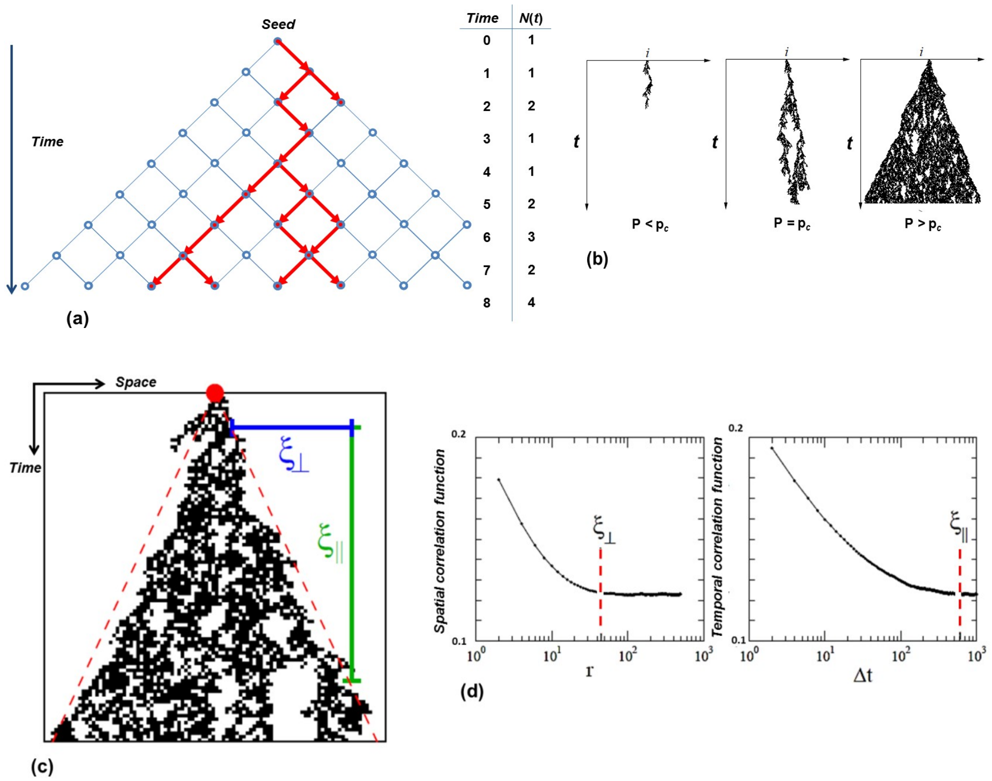
[4] We define the *correlation length* in Chapter 9.

length, $\xi_{\|}$, (Figure 5.4 c). It is found that these parameters scale according to distance from criticality as:

$$\begin{aligned} \rho &\sim \left(p - p_c\right)^{\beta} \\ \xi_{\perp} &\sim \left(p - p_c\right)^{-\nu_{\perp}} \\ \xi_{\|} &\sim \left(p - p_c\right)^{-\nu_{\|}} \end{aligned} \qquad (5.3)$$

where β, $\nu_{\perp}$, $\nu_{\|}$ are known as *critical exponents* and $\sim$ is meant to be read as *asymptotically proportional to*; in general the critical exponents are not integers. See Hinrichsen (2005) for a discussion of the values of these exponents for this model. Notice that the correlation lengths diverge to infinity at criticality. This kind of behaviour is a defining characteristic of equilibrium critical (continuous) phase transitions and it seems from this well studied example that it can also occur for non-equilibrium phase transitions as well.



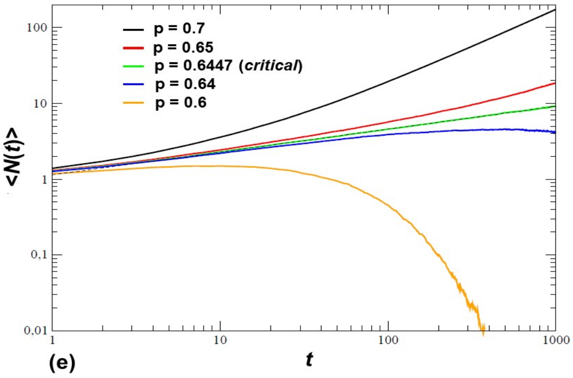


Figure 5.4. The directed flow (or bond) percolation model. (From Hinrichsen, 2005). (a) The model with active links in the lattice shown in red. The table on the right hand side of (a) gives the number, $N(t)$, of active nodes at a given time-step. (b) Maps of the percolation for various values of the probability, p, of a lattice bond being active. p_c is the probability at criticality. (c) Map of the system for $p > p_c$. The directions in which the correlation lengths, $\xi_\perp$ and $\xi_{||}$ are measured are shown. (d) The spatial and temporal correlation functions plotted against distance, r, and time difference, Δt. In both cases the correlation function decreases until it levels off at the respective correlation lengths, $\xi_\perp$ and $\xi_{||}$. (e) Plot of the logarithm of the average of $N(t)$) against time for various values of p. Critical p_c is identified as the transition between exponential decay for $p < p_c$ and (ultimately) linear growth for $p > p_c$.

In Figure 5.4 (e) the average of the quantity, $N(t)$, (defined in Figure 5.4 a), is plotted as a log-log plot against time for various values of the probability, p. At criticality, corresponding to $p = 0.6447$, the behaviour is asymptotic to power-law behaviour; for $p < 0.6447$, $N(t)$, first increases slightly and then decreases exponentially; the transition from slow growth to exponential decay depends on the distance from criticality, $(p - p_c)$. For $p > 0.6447$ the behaviour is first slow and then increases to a linear function of time. The behaviour depicted in Figure 5.4, and also expressed by the system of equations (5.3), is classical behaviour for any equilibrium critical system undergoing a continuous phase transition and is reproduced here for a non-equilibrium system. Such behaviour needs to be demonstrated for any system in order to attach the term *critical* to its behaviour.

The behaviour of complex systems undergoing a continuous phase transition displays a feature that is common across all such systems no matter how different the individual processes and dynamics may be. This property is called *universality*. One aspect of universality is that exponents such as β, $\nu_\perp$ and $\nu_{||}$ in (5.3) are the same for many systems independently of the detailed processes that operate. One goal of a study of hydrothermal systems is to establish these exponents for hydrothermal systems and see if such exponents are the same as in other common classes of critical systems. Another aspect of universality is that the emergent phenomena do not exhibit a characteristic length or time scale. The result is that behaviours both in space or time look similar at all scales of observation. Thus the system reveals structure within structure over a large range of scales. Such behaviour is called *fractal*.

The only mathematical equation[5] that expresses the probability of occurrence, $p(r)$, at a scale, r, that does not change its form as r is varied is a power law:

$$p(r) = \beta r^{-\alpha} \qquad (5.4)$$

where β is a constant and α is a number not necessarily an integer. If we change r to $2r$ then we obtain

$$p(2r) = \beta\left(2^{-\alpha}\right)r^{-\alpha} = \beta^{/} r^{-\alpha}$$

which is of the same form as (5.4). Thus fractal geometries or time series follow power law statistics. We will examine fractal geometries more closely in Chapter 6.

5.4 Phase transitions.

A system is said to undergo a phase transition when there is a system wide change in the qualitative behaviour of the system at the macroscopic level. Most studies of phase transitions involve equilibrium phase transitions and these have been extensively studied both experimentally and theoretically since van der Waals (see Kondepudi and Prigogine, 1998). In the classical view of phase transitions, a phase transition is said to be of order n if the n^{th} derivative of the energy with respect to the temperature does not exist whereas the $(n+1)^{th}$ derivative does exist. Thus for the water → steam transition the first derivative of the Gibbs energy, G, (or the chemical potential for a pure chemical system) does not exist at the transition whereas the second derivative (the entropy) does exist. This transition is abrupt. On the other hand, in the transition: critical H_2O → subcritical H_2O the second derivative of the Gibbs energy (or the chemical potential) does not exist whereas the third derivative (the specific heat) does exist. This transition is continuous. Examples of the attributes of the two common classes of equilibrium phase transitions ($n = 1$ and $n = 2$) are given in Figure 5.3. This classical view is somewhat misleading since "second order" transitions do not behave as shown in Figure 5.3 (right hand column) but rather show scaling behaviour as criticality is approached. The terms *abrupt* and *continuous* tend to be used instead of first and second order. However there exists a bewildering array of *non-equilibrium* phase transitions that have been the subject of considerable theoretical study and computer simulation but relatively little in the way of experimental investigation. An open question is: *Do these non-equilibrium phase transitions behave in the same way as equilibrium phase transitions?*

5.4.1. Equilibrium phase transitions.

Equilibrium phase transitions are commonly classified as first order (or abrupt) phase transitions or second order (or continuous) phase transitions. The classical distinction between these two types of transitions is illustrated in Figure 5.3. Examples of *abrupt* phase transitions are most of the common chemical reactions in metamorphic petrology where a jump (or discontinuity) in quantities such as the volume or the heat of reaction occurs. These are normally quoted as the ΔV or ΔH of the reaction (figure 5.3 a, c). Some measure of the energy of the system (in Figure 5.3 e, the chemical potential) is continuous at the phase transition but its derivative with respect to temperature (the entropy) is discontinuous (Figure 5.3 g). The standard example of an

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[5] See Newman (2006) for an in depth discussion of power laws.

equilibrium *continuous* phase change is the supercritical → water + steam transition where the entropy is continuous at the critical point and $\Delta V = \Delta H = 0$.

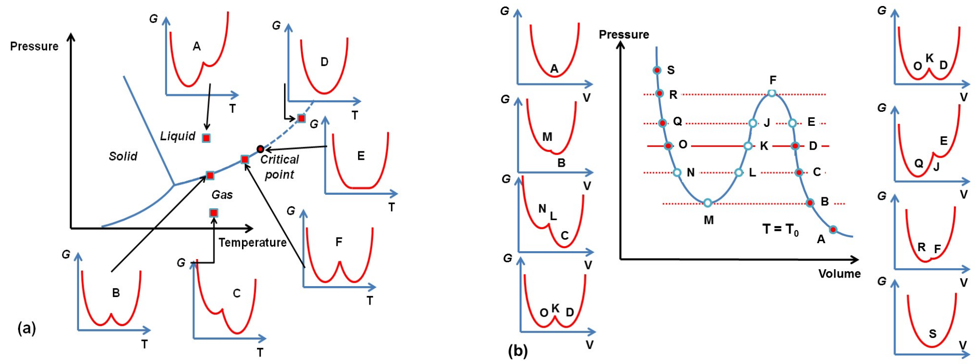


Figure 5.5. Phase transitions in a liquid → gas phase change. (a) The Gibbs energy of the system for various pressure (P) and temperature (T) conditions The Gibbs energy nearing a phase boundary is non-convex except for the super-critical phase at D where it is convex. At the critical point (E) the Gibbs energy is flat bottomed. Elsewhere the Gibbs energy is non-convex and consists of two minima, one (to the left) corresponds to the liquid phase and the other (to the right) corresponds to the gas phase. At the phase boundary (B and F) the two minima occur at the same Gibbs energy. Elsewhere (A and C) the Gibbs energy is asymmetrical reflecting the relative proportions of liquid and gas. In these instances the phase corresponding to the highest minima is meta-stable. (b) The same information as in (a) but plotted in (Gibbs energy – volume)-space at a constant temperature, $T = T_0$. At A there is one phase and it is super-critical and stable. As one progresses along the isotherm, $T = T_0$, from A one meets stable phases, B and C, which coexist with meta-stable phases, M and N. At D a stable phase coexists with another stable phase, O. E and F are meta-stable phases that coexist with stable phases, Q and R, Finally, S is a stable phase (Adapted from Ortin, 1997).

The classical example of an abrupt transition is the water → steam transition and is explored further in Figure 5.5. Here a heated container of water changes to a mixture of steam and water at a temperature called the boiling point, T_B. The same water → steam transition could also be obtained by maintaining a constant temperature and decreasing the pressure. The phase transition water → steam is characterised by a control temperature or a control pressure. The explanation of what is observed lies in the system evolving towards a state of minimum energy. At temperatures below the boiling point the energy of the system is represented by the plots of Gibbs energy against temperature shown in Figure 5.5 (a); this plot consists of two humps (the energy is said to be *non-convex*) with minima corresponding to the two phases, water and steam. At (P-T) conditions where water is stable, the minimum corresponding to water is lower (configuration A in Figure 5.5 a) so that the system consists of (stable) water with bubbles of (metastable) steam. At the phase boundary both minima are at the same level (configuration B) so that the system consists of a mixture of (stable) water and (stable) steam. The concentration of the metastable phase decreases exponentially with the distance from T_B but the presence of the metastable phase is fundamental in providing nuclei for growth of the new phase at the transition. Under conditions where steam is the stable phase the plot of Gibbs energy against temperature is again asymmetrical (configuration C) but in the opposite sense so that the system consists of a mixture of (metastable) water in (stable) steam. The transition from (metastable steam plus stable water) to (stable steam + stable water) takes place by a nucleation plus growth process. In abrupt transitions the size of new grains, R, grows with time, t, according to $R \sim t^{1/2}$, R

$\sim t^{1/3}$, $R \sim t^{1/4}$, according to whether the growth is controlled by diffusion in a fluid, surface diffusion or bulk diffusion respectively. In addition, the grain size distribution is self-similar from one time to another (Zollner and Streitenberger, 2008).

In Figure 5.5 (b) this transition is viewed from another perspective where each state is seen as a section across (P – V) - space in (Gibbs energy – volume) – space at a constant temperature, T_0. Each full dot in Figure 5.5 (b) represents a stable phase whereas each empty dot is an unstable or metastable phase.

The abrupt transition, water → steam, illustrated in Figure 5.5 (a) contrasts with the continuous transition: supercritical H_2O → water + steam (configurations D, E and F in Figure 5.5 a) where the plot of Gibbs energy versus temperature is convex for supercritical H_2O (configuration D), remains convex at the critical point but has a broad base (configuration E) and becomes non-convex but symmetrical after the critical point (configuration F). The transition is smooth and does not involve a change in volume or heat of transformation. Nor does it involve a nucleation-growth process that depends on the competition between Gibbs energy reduction and increase in surface energy. The system begins to organise as the transition is approached and the development of a new phase is a cooperative process whereby regions of the new phase begin to form throughout the system and the presence of the new phase is such as to encourage the development of more of the new phase. The result is the presence of the new phase within the old phase at all spatial scales. The transition however is associated with a number of scaling phenomena we will elaborate upon below. Universally it is observed that when the control parameter reaches a specified value the system develops long range order so that domains of one phase or the other exist at all scales with no preferred length scale exhibited. This is an expression of the flat base to the Gibbs energy function at the critical point which is expressed as a wide range of density fluctuations. This behaviour is commonly referred to as *scale invariance*.

The important feature that distinguishes an abrupt from a continuous phase transition is that in an abrupt transition parameters characteristic of the transition (such as the concentration of metastable phases) decrease exponentially away from the transition whereas in a continuous transition parameters characteristic of the transition scale in a power-law manner in approaching the critical point that represents the transition.

5.4.2. Non-equilibrium phase transitions.

The classical view of phase transitions illustrated in Figures 5.4 and 5.5 is meant to apply to equilibrium phase transitions and pervades the literature devoted to equilibrium thermodynamics. However there are a vast number of non-equilibrium phase transitions and the interest lies in establishing the characteristics of these transitions. The subject is very much in its infancy largely because of the lack of well documented examples and the difficulty of conducting experiments but some principles are apparent. Below we explore two examples, one of a non-equilibrium abrupt transformation and the second of a continuous transformation.

An example of a non-equilibrium phase transition that resembles an abrupt transition is given by a form of the Kaplan-Yorke map (Beck and Schlögl, 1993) expressed as:

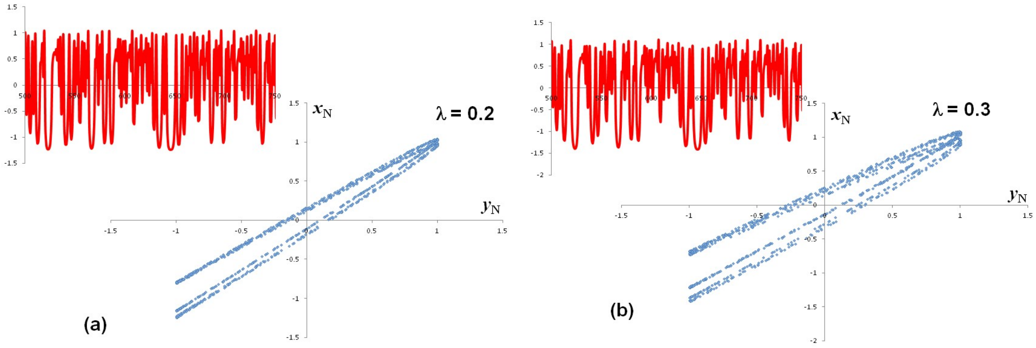
$$\begin{aligned} x_{n+1} &= 1 - 2x_n^2 \\ y_{n+1} &= \lambda y_n + x_n \end{aligned} \tag{5.5}$$

This map exhibits chaos as shown in Figure 5.6. As λ is varied from 0.2 to 0.9 the attractor changes from a set of closely nested fractal horse-shoe shaped structures to a widely dispersed structure that widens as λ increases. The phase transition occurs at $\lambda = 0.5$. The abrupt nature of this transition is shown in the behaviour of the Rényi dimensions, D(β, λ) (Beck and Schlögl, 1993, pp 267-272). In Chapter 6 we see that the Rényi dimensions represent energy levels in statistical mechanics whilst β can be taken to be the reciprocal of the statistical temperature. In this interpretation λ, which is the parameter in (5.5), represents some other external control parameter imposed on the system. An example might be pH for instance. Thus Figure 5.7 (a) is a (1/T, pH) phase diagram whereas Figures 5.7 (b) and (c) are plots of energy versus pH at constant T, and energy versus (1/T) at constant pH respectively.

The Rényi dimensions, D(β, λ) are given by (Beck and Schlögl, 1993, pp 267-272):

$$D(\beta,\lambda) = \left| \begin{array}{ll} 1+\dfrac{\ln 2}{\left|\ln\lambda\right|} & \mathit{for}\ \lambda \le \dfrac{1}{2}, \beta \le 2 \\ \dfrac{\beta}{2(\beta-1)}+\dfrac{\ln 2}{\left|\ln\lambda\right|} & \mathit{for}\ \lambda \le \dfrac{1}{2}, \beta \ge 2 \\ 2 & \mathit{for}\ \lambda \ge \dfrac{1}{2}, \beta \le 2 \\ 1+\dfrac{\beta}{2(\beta-1)} & \mathit{for}\ \lambda \ge \dfrac{1}{2}, \beta \ge 2 \end{array} \right.$$

These relations are shown in Figure 5.7. Clearly there are discontinuities in the Rényi dimensions at $\lambda_{\text{transition}} = 0.5$ (Figure 5.7 b) and $\beta_{\text{transition}} = 2$ (Figure 5.7 c) which act as *transition lines* defining an abrupt phase transition.



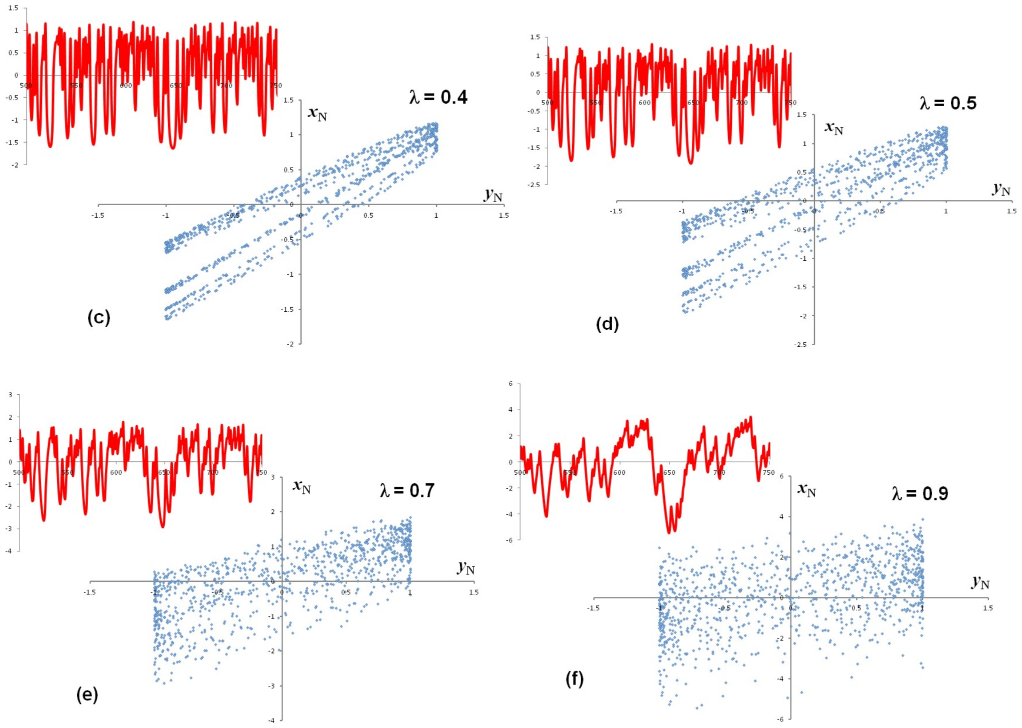
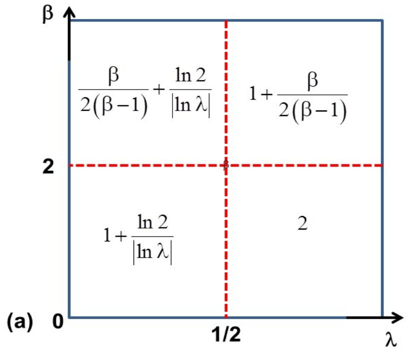


Figure 5.6. An abrupt phase transition in the Kaplan-Yorke Map given by (5.5) with initial values of $x_0 = y_0 = 0.1$. The attractor for each value of λ in (5.5) is shown for the first 1000 iterations together with the signal produced for the iterations between 500 and 750 steps. An abrupt phase transition occurs λ = 0.5 (frame d) where the attractor and the signal change character. There is no scaling associated with the attractor of the signal that marks the phase change.



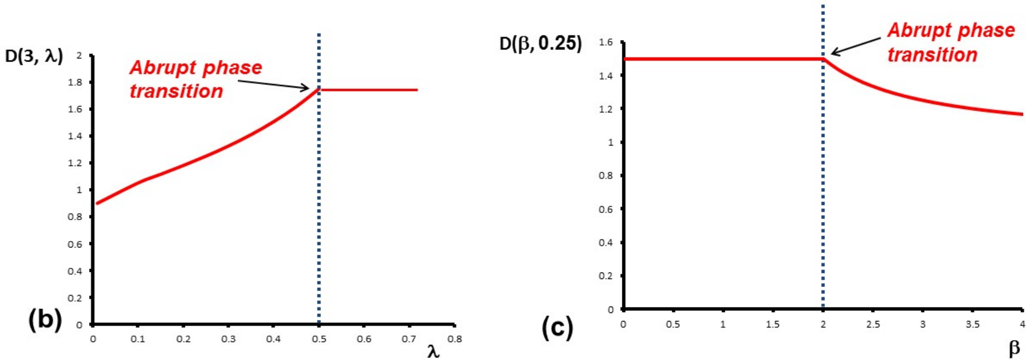
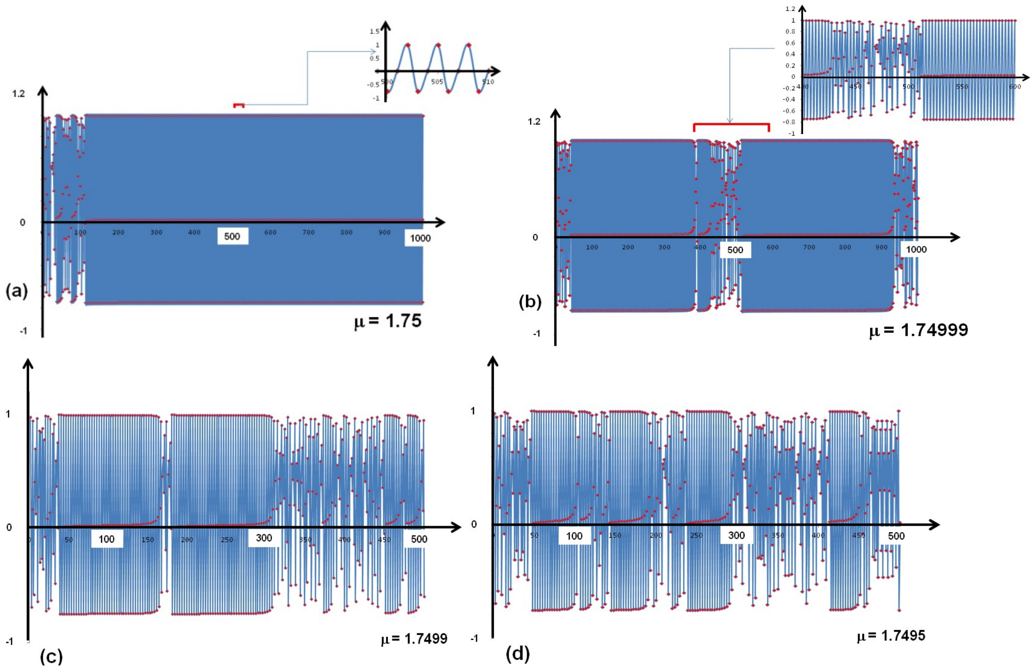


Figure 5.7. Phase diagram for the Kaplan-Yorke map (5.5) illustrated in Figure 5.6. (a) Fields showing the value of D(β, λ) as a function of λ and β. (b) A section across (a) at β = 3. An external abrupt phase transition is indicated. (c) A section across (a) at λ = 0.25. Another (internal) abrupt phase transition is indicated. Notice that scanning across β is equivalent to scanning across 1/T.

An example of a non-equilibrium continuous phase transition occurs in the logistic map, (5.1), as a critical value of the parameter, μ, $\mu_c = 1.75$, is approached from below (Figure 5.8). As one approaches the transition, chaotic behaviour gives away to intermittancy with packets of periodic behaviour alternating with packets of chaotic behaviour (Figure 5.8). This lamellar structure coarsens as one appoaches the transition until at $\mu_c = 1.75$ the behavour is completely periodic after the first transients (Figure 5.8 a). The lamella thickness , L , scales (Beck and Schlögl, 1993) as

$$L \approx \left(\mu - \mu_c\right)^{-\delta}$$

This power-law type of scaling behaviour is the defining feature of equilibrium continuous transitions and seems to be a feature of many non-equilibrium transitions as well (Cross and Greenside, 2009).



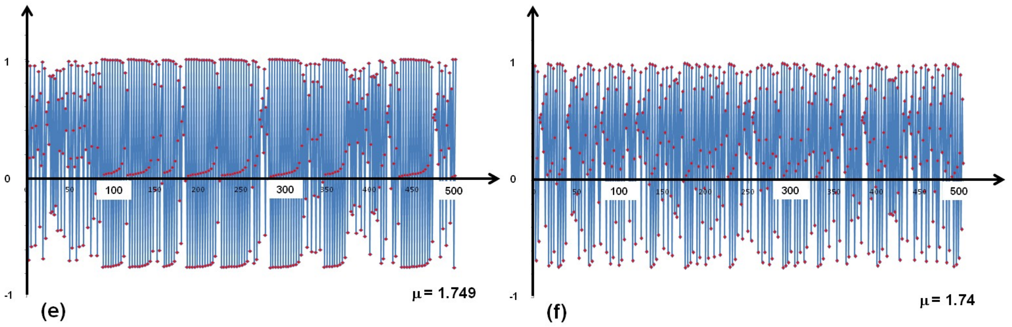


Figure 5.8. A continuous phase transition associated with intermittency in the logistic map: $x_{N+1} = 1 - \mu x_N^2$. The figures show the scaling of the width, L, of the *lamella phase* proceeding towards a critical point at $\mu = 1.75$. The change of scale for (a) and (b) as opposed to (c) to (f) is because the scaling is a power law: $L \approx \left(\mu_{critical} - \mu\right)^{-\delta}$ and so the lamella thickness increases dramatically as the critical point, $\mu = 1.75$ is approached from below. (a) $\mu = 1.75000$ first 1000 iterations. (b) $\mu = 1.74999$ first 1000 iterations. (c) $\mu = 1.7499$, first 500 iterations. (d) $\mu = 1.7495$, first 500 iterations. (e) $\mu = 1.749$, first 500 iterations. (f) $\mu = 1.74$, first 500 iterations. In these diagrams, the point arising in each iteration is shown as a red diamond and the lines connecting successive points in blue.

5.4.3. Topological interpretations of phase transitions and chaos.

Although conceptually abstract it may be of benefit to some readers to explore the topological approach to Nonlinear Dynamics. This view of dynamical systems unifies much of the subject. Here the various states that an evolving system can occupy are taken as defining a region of phase space called a *manifold* (Ivancevic and Ivancevic, 2008). If the system is linear this manifold is planar with no curvature. Nonlinear dynamical systems are characterised by curved manifolds. Chaos in nonlinear dynamical systems is marked by a topological change in the manifold to a new manifold that cannot be transformed to the old manifold by a distortion; the two manifolds can only be transformed to each other by cutting, distorting and joining.This difference in manifold topology is called *diffeomorphism*. Examples are the transition from a sphere to one or more tori (figure 5.9). The change in topological character marks a phase transition in many systems and the change also marks a transition from a stable nonlinear system to a chaotic system. For details see Ivancevic and Ivancevic (2008) although the mathematics is not simple.

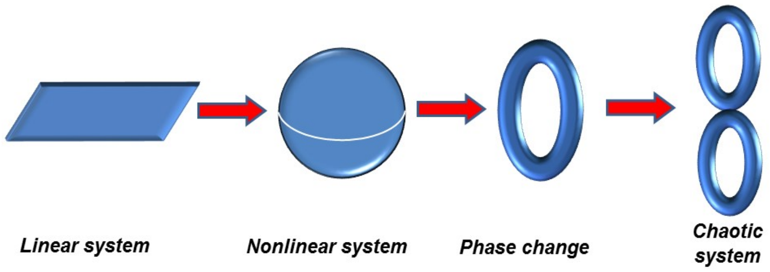


Figure 5.9. Sketch of some topological representations of linear, nonlinear and chaotic systems and phase changes. Each of the systems is represented by a manifold which is a region in phase space that contains all states of the system. A linear system always occupies a planar manifold. A nonlinear system occupies a curved manifold (in this case a sphere). Chaos occurs when the manifold changes to a topologically distinct manifold (such as two connected tori that cannot be transformed topologically into a sphere). A phase change is at the boundary between two topologically distinct manifolds (in this case at the boundary between a spherical and a torical manifold). For detailed discussion see Ivancevic and Ivancevic (2008).

5.5 Phase transitions and bifurcations.

The two concepts, *phase transition* and *bifurcation*, are used to describe a system-wide qualitative (and commonly quantitative) change in state. Such changes in both cases may be described by terms such as from *disordered to ordered*, *homogeneous to heterogeneous*, *unpatterned to patterned*, *homogeneous to localised*, *un-fractured to fractured*, *one mineral phase or assemblage to another*, *un-mineralised to mineralised*, *unaltered to altered*, *impermeable to permeable*, *planar layering to folded layering*, *stationary conductive to convective fluid flow*, *elastic to plastic*, *intact to brecciated*, and a host of others. Formally, (Figure 5.10 a), a phase transition marks a change from a convex to a non-convex energy function whereas a bifurcation point is marked by a change in the mathematical character of the governing equations for the system. Formally, a necessary condition for a bifurcation (Wiggins, 2005) is that the governing equations pass from elliptical to hyperbolic, commonly referred to as a *loss in ellipticity*.

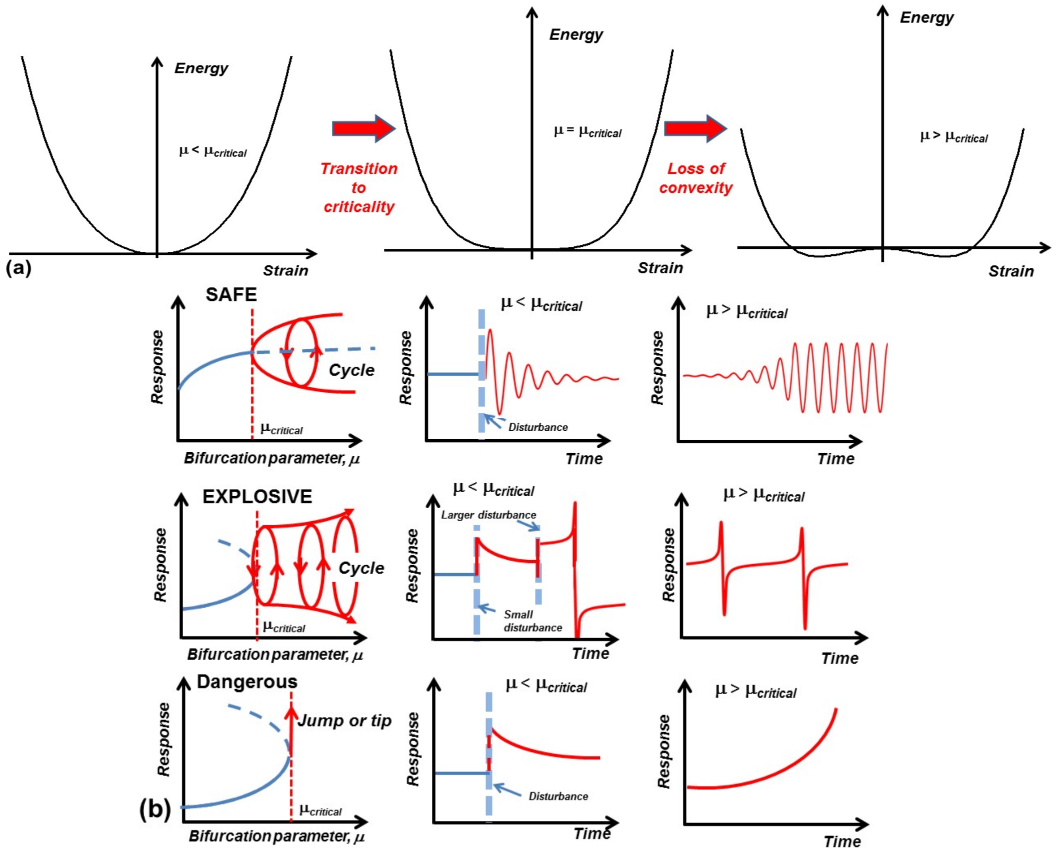


Figure 5.10. Two ways that a system can become unstable. (a) Loss of convexity. The energy function paases from strictly convex away from criticality to convex with a wide base at criticality to double humped (non-convex) as criticality is passed. (b) In a mechanical system, loss of ellipticity. The three types of bifurcation, safe (top row), explosive (middle row) and dangerous (bottom row) are illustrated. On the left the bifurcation parameter or time is plotted horizontally and the response of the system vertically. In the middle column the responses of the systems below the critical value of the bifurcation parameter are plotted following a disturbance. In the right hand column the response of the systems after the critical bifurcation parameter is passed are plotted.

5.5.1. Classification of bifurcations.

Bifurcations have been classified by Thompson et al. (1994) and Thompson and Sieber (2010). Aspects of this classification are illustrated in Figure 5.10 (b) and Table 5.3. Three broad classes of bifurcations are recognised, namely, *safe*, *explosive* and *dangerous* bifurcations; they have the following characteristics:

- *Safe bifurcations:* The bifurcation is subtle and continuous with no fast jump to another attractor set. The process is deterministic with a single outcome independent of any noise in the system. There is no hysteresis so that the process is reversible. No intermittency is observed. The coarsening of the lamella phase in the logistic map illustrated in Figure 5.8 is an example of a safe bifurcation. Sethna (2006, p 283) identifies a continuous phase transition with a safe bifurcation as does also Sornette (2008, p 256). Thus there are examples where a safe bifurcation and a continuous phase transition are corresponding concepts. Precursors to safe bifurcations are discussed by Sornette (2008, his chapter 10).
- *Explosive bifurcations:* The bifurcation is catastrophic with an abrupt enlargement of the same attractor set. The process is deterministic with a single outcome independent of any noise in the system. Intermittency can be observed especially as the old regime is left behind. Sornette (2008, p262) identifies an abrupt phase transition with an explosive bifurcation.
- *Dangerous bifurcations:* The bifurcation is catastrophic with sudden disappearance of the old attractor and a sudden jump to a new (unpredictable) attractor set (Figure 5.10 b). Hysteresis exists so that the reverse path is not followed. No intermittency occurs but a global slowing of the response may occur. This seems to be the type of bifurcation envisaged by climate modellers when they speak of a *tipping point* (see Thompson and Sieber, 2010).

In the above discussion some correlations between phase transitions and bifurcation phenomena have been made. However this is not always the situation and if we want a deep understanding of hydrothermal systems we need to be able to distinguish between phase transition and bifurcation behaviour. The situation is not made easy by the fact that processes other than phase transition and bifurcation behaviour can result in a change in the character of the system. Even if the only two alternatives are a loss in convexity or a loss in ellipticity then for some systems both may occur together whilst in other systems one can occur before or after the other.

Table 5.1. Phase transitions and bifurcations compared.

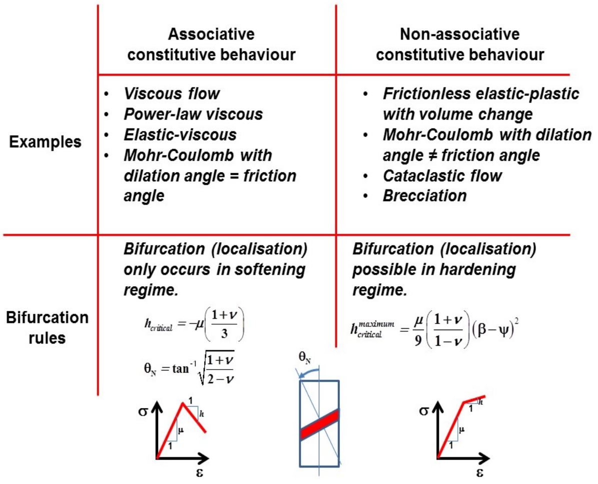
Phase transition	**Bifurcation**
System changes in qualitative behaviour.	System changes in qualitative behaviour.
An energy function changes from convex to non-convex at a point controlled by some system parameter (referred to as *loss in convexity**).	The mathematical equations change character at a bifurcation point controlled by some system parameter (referred to as *loss in ellipticity**).
At a phase transition heterogeneities show long range correlations with no characteristic length scale (the probability distributions are fractal-called *heavy tailed*).	At a bifurcation some form of spatial and/or temporal patterning commonly develops arising from competition between two or more processes. Long range correlations may arise because of regular pattern formation.
Depending on whether the phase transition is abrupt or continuous, various parameters that	Some bifurcations are smooth (*safe bifurcations*), some are abrupt (*explosive*

characterise the phase transition do not, or do, show scaling as the phase transition is approached with divergence of these properties at the phase transition.	*bifurcations*) and some completely discontinuous (*blue sky or dangerous bifurcations*). Some of these bifurcations show precursory behaviour, others do not (Thompson et al., 1995; Thompson and Sieber, 2010).
If the transition shows this characteristic scaling then the phase transition is critical and defined by a critical point (or line/plane in some transitions)	The smooth bifurcations have been compared with continuous transitions and the explosive bifurcations with abrupt transitions. (Sornette, 2008, p 256)

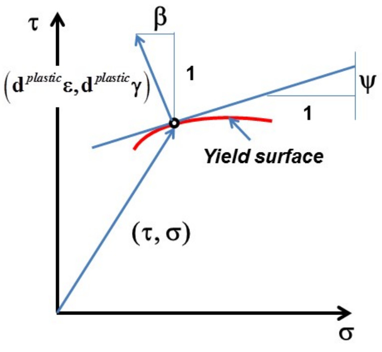
[*] In some systems loss of convexity precedes loss in ellipticity. In others the reverse situation occurs (Lyakhovsky et al., 2008; Rudnicki and Rice, 1975).

The localisation of strain in the form of a shear band in an elastic-plastic material has been examined as a bifurcation problem by Rudnicki and Rice (1975) for isotropic elasticity and for anisotropic elasticity by Bigoni and Loret (1999). The result is that for materials such as metals and rocks at high pressures and temperatures where there is no volume change during deformation and no dependence of the flow stress on pressure (that is, no frictional effects), bifurcation leading to localisation must always occur during strain-softening. Such materials are said to have *associative constitutive behaviour*. For materials that show frictional effects (a dependence of flow stress on mean stress) a *frictional coefficient*, ψ, can be defined as in Table 5.2. In addition a dilation coefficient, β, can be defined as in Table 5.2. If $\beta = \psi$ the material is said to be *associative*, otherwise the material is *non-associative*. For non-associative materials bifurcation leading to localisation is possible in the hardening regime. These relations are summarised in Table 5.2. Lyakhovsky et al. (2008) present a model of localisation involving a material with nonlinear elasticity. This results in localisation arising from a loss in convexity occurring before bifurcation that arises from the Rudnicki and Rice bifurcation analysis.

Table 5.2. Characteristics of bifurcations corresponding to shear localisation in associative and non-associative materials with isotropic elasticity. ν is Poissons ratio, μ is the elastic slope and h is the plastic hardening modulus.



	Associative constitutive behaviour	Non-associative constitutive behaviour
Examples	- *Viscous flow* - *Power-law viscous* - *Elastic-viscous* - *Mohr-Coulomb with dilation angle = friction angle*	- *Frictionless elastic-plastic with volume change* - *Mohr-Coulomb with dilation angle ≠ friction angle* - *Cataclastic flow* - *Brecciation*
Bifurcation rules	*Bifurcation (localisation) only occurs in softening regime.* $h_{critical} = -\mu\left(\frac{1+\nu}{3}\right)$ $\theta_N = \tan^{-1}\sqrt{\frac{1+\nu}{2-\nu}}$	*Bifurcation (localisation) possible in hardening regime.* $h_{critical}^{maximum} = \frac{\mu}{9}\left(\frac{1+\nu}{1-\nu}\right)(\beta-\psi)^2$



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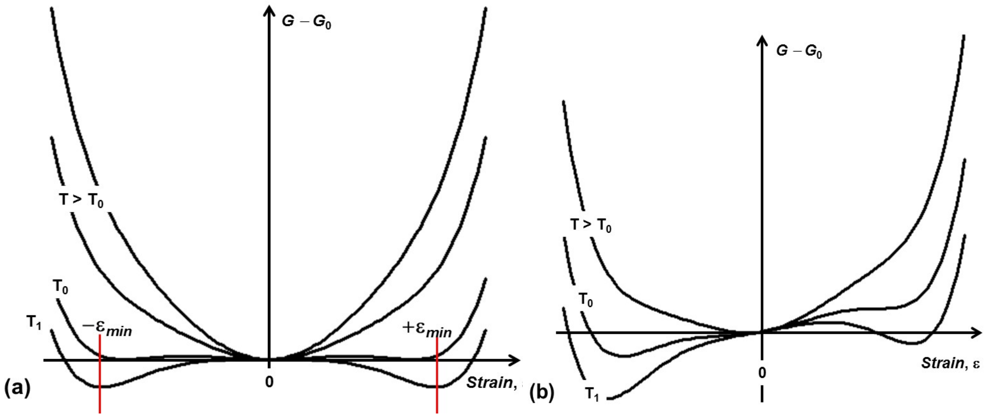
As an example of a system where loss of convexity may proceed, coincide or post-date loss of ellipticity consider the mechanical system discussed by Ortin (1997). He proposes a system where the Gibbs energy, *G*, of the mechanical system is given in terms of temperature, T, pressure , P, and uniaxial strain, ε, by a power law of the form:

$$G(\mathrm{P},\mathrm{T},\varepsilon) = G_0(\mathrm{P},\mathrm{T},\varepsilon) + A\varepsilon^2 - B\varepsilon^4 + C\varepsilon^6 \qquad (5.6)$$

where *A* is a function of temperature, $A = a(\mathrm{T} - \mathrm{T}_1)$, and *a*, *B*, *C*, T_1 are positive constants. The functional form of (5.6) has been chosen with no odd powers for symmetry reasons so that a change in sign of ε does not change the form of *G* and the powers provide for the existence of three minima. G_0 is the Gibbs energy at some reference state. The behaviour of $(G - G_0)$ as a function of strain is shown in Figure 5.11. The behaviour in Figure 5.11 (a) represents an abrupt phase transition and this type of system was first explored by Landau; for a complete exposition of the Landau theory see Toledano and Toledano (1987).

We consider three regions in Figure 5.11 (a). Above a temperature, $\mathrm{T}_{0,}$ there is one minimum in the function indicting there is only one stable deformation, namely ε = 0; it is possible to develop metastable deformations as the temperature decreases towards T_0 (see Ortin, 1997). Decreasing the temperature in the region, $\mathrm{T}_1 \le \mathrm{T} \le \mathrm{T}_0$, deepens the minima that appear. Each minimum corresponds to a different strain, labelled $\pm\varepsilon_{min}$ (Figure 5.11 a) so that the deformations at these two strains become stable and the deformation at ε = 0 is metastable. Decreasing the temperature below T_1 (not shown) makes the deformation at ε = 0 unstable.



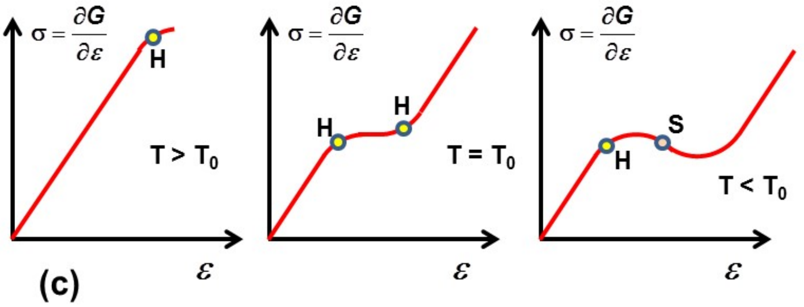


Figure 5.11. A model (inspired by Ortin, 1997) demonstrating some possible relations between loss of convexity and loss of ellipticity. (a) A Landau model showing the variation with temperature of the Gibbs energy with strain with no imposed stress. T_0 corresponds to a temperature where three minima occur in the Gibbs energy and corresponds to loss of convexity: For temperatures above T_0 there is only one minimum and the energy function is convex; for temperatures below T_0 there are two minima symmetrically disposed with respect to zero strain and the energy function is non-convex. (b) The Gibbs energy with an imposed stress which changes the symmetry of the system. (c) Sketches of stress-strain curves that result from the situation in (b) for $T > T_0$, for $T = T_0$ and for $T < T_0$. Possible bifurcation points are indicated (arising from loss of ellipticity) depending on whether bifurcation occurs in the Hardening regime (H) or the Softening regime (S). For a detailed discussion of many aspects of this model see Ortin (1997).

If we increase the stress, σ, above zero (5.6) can be written in its simplest form as:

$$G(\mathrm{P,T},\varepsilon)=G_0(\mathrm{P,T},\varepsilon)+A\varepsilon^2-B\varepsilon^4+C\varepsilon^6-\sigma\varepsilon \qquad (5.7)$$

The symmetry of Figure 5.11 (a) is now broken so that the Gibbs energy is represented in Figure 5.11 (b). We make use of a result in the thermodynamics of mechanical systems (see Hobbs and Ord, 2015) that says that the stress is the differential of the Gibbs energy with respect to the strain:

$$\sigma=\frac{\partial G}{\partial\varepsilon}$$

Thus the stress-strain curves corresponding to $T > T_0$, $T = T_0$ and $T < T_0$ may be plotted as in Figures 5.11 (c), (d) and (e) respectively. Localisation, following the Rudnicki and Rice approach can now occur in the hardening regime (labelled H in Figure 5.11) if the material is non-associative or in the softening regime (labelled S) if the material is associative. Thus localisation can occur before, at or after criticality for non-associative materials but only after criticality for associative materials.

An example of a continuous phase transition is given by Ortiz (1999) where the plastic yield of materials is viewed as a *continuous phase transition in which the Helmholtz energy* undergoes a transition from *convex* to *non-convex* (Figure 5.12). Ortiz (1999) for instance describes the plastic yield of metals in terms of an energy function derived for a very simple deformation mechanism where the glide of a single dislocation is inhibited by forest dislocations that intersect the glide plane. The energy, $f(h_0)$, is plotted for various temperatures against a measure of the strain, h_0 in Figure 5.12 (a). The energy passes through a transition from non-convex to convex at a critical temperature T_{crit}. Ortiz (1999) shows that quantities such as the dislocation density and the plastic compliance, $\left(\frac{\partial\tau}{\partial\gamma}\right)_{\mathrm{T}}$, scale in a manner identical to the behaviour of a continuous phase transition as the critical temperature is approached. Here τ is the shear stress and γ is the shear strain.

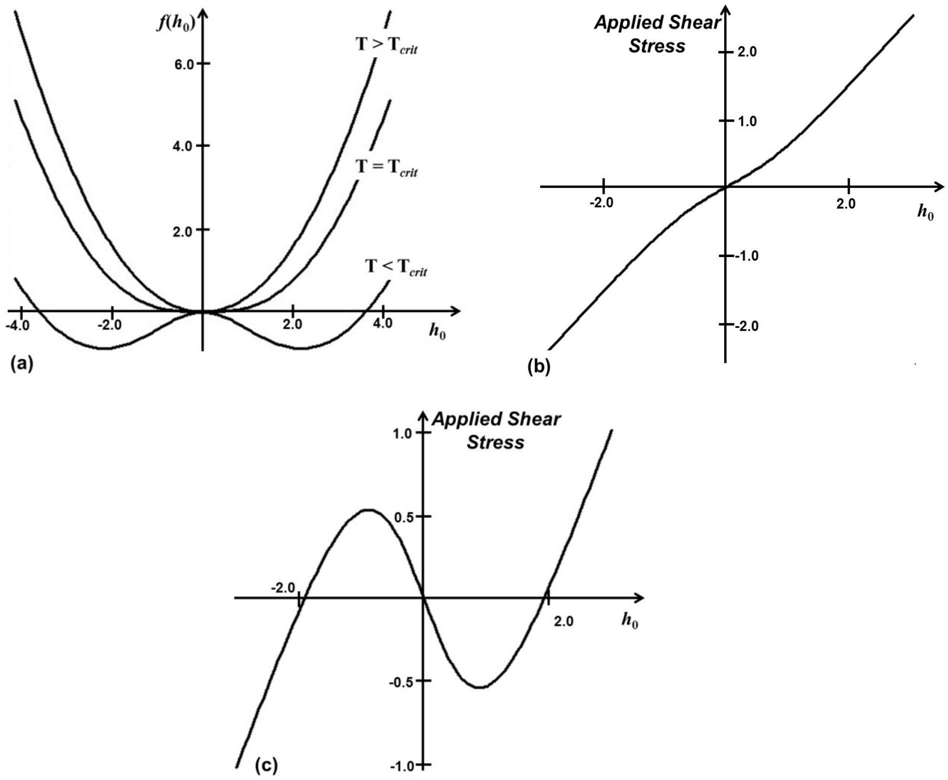


Figure 5.12. A critical transition corresponding to plastic yielding as a function of temperature. From Ortiz (1999). (a) The transition between a convex energy function for T > T_{crit} to a non-convex function for T < T_{crit}. (b) Stress strain curve for T > T_{crit} where the strain is measured by h_0. (c) Stress strain curve for T < T_{crit} where the strain is measured by h_0.

The derived stress strain curves are shown in Figure 5.12 (b) and (c) for T > T_c and for T < T_c respectively. Since this model involves dislocation interactions (so the constitutive behaviour is non-dilatant) localisation (loss of ellipticity) can only occur in the softening regime and so in decreasing the temperature, loss of convexity occurs before loss in ellipticity.

5.5.2. Self-organised criticality. Threshold dynamics.

The concept of criticality has been made popular by Bak (1996) who proposed that some systems when gently forced from an equilibrium state ultimately reach a threshold where some kind of scale independent phenomenon emerges. This phenomenon was christened *self-organised criticality* by Bak and co-workers (Bak, Tang and Wiesenfeld, 1987). The archetype example proposed was the slow loading of a sand-pile until a scale independent pattern of avalanches emerges. This behaviour (the best examples of which appear in computer experiments and not in natural systems) was proposed as one example of critical behaviour although the precise physics behind the process has never been enunciated. Experimental examples of self-organised criticality have been reported from piles of specially elongated rice grains.

The concept called *self-organised criticality* is given some detailed discussion by Sornette (2006). He gives the following criteria for self-organised criticality:

- The system is driven at a constant very slow rate and composed of many interacting components.
- The system has highly nonlinear behaviour with essentially a threshold response.
- The threshold corresponds to a globally stationary state, characterised by a stationary probability distribution.
- These probability distributions are power-law in nature with fractal geometries and long-range correlations.

As we have indicated we do not use the term *self-organised* because it tends to give the system the responsibility and ability to organise itself and hence commonly implies there is no further need for explanation.

The problem with the use of the term *self-organised criticality* (SOC) is that the concept is loosely defined. As indicated above, Sornette (2006) has offered some criteria that characterise SOC but no mechanisms based in physics or chemistry are offered. The issue is that all of the four criteria offered by Sornette can arise from other processes including abrupt phase changes (non-critical), second order phase changes (critical) and many phenomena associated with bifurcation (non-critical). One could ask the following questions that embrace the hallmarks of criticality: *Is SOC like a continuous phase transition that involves the evolution of heterogeneities described by scaling exponents*? *Does SOC involve a loss in convexity for an energy function*? *Does SOC involve the minimisation of an energy function*? *SOC clearly is a non-equilibrium phenomenon so is the stationary state mentioned in Sornette's list a super-critical state*? *How would I distinguish a SOC system from one undergoing a first or continuous transition*? As far as we are aware there are no answers to these questions which is why the concept is so loosely defined. Due to the lack of constraints on the concept an SOC system can behave in any manner the proponent wishes (subject to Sornette's list). In a way, SOC systems resemble the concept of mantle plumes. They also can behave in any way the proponent wishes. One should read the paper by Lundin (2013): *Plumes do that*. The sentiments expressed by Lundin are directly applicable to the SOC concept as it is presently defined and applied.

However, we believe a working definition of SOC is: SOC is exhibited by a system that is continuously forced to either remain in a critical state or to continuously revisit a critical state. Here we use the term *critical* in its strict meaning as a state of a system that exhibits long range correlations and a fractal geometry.

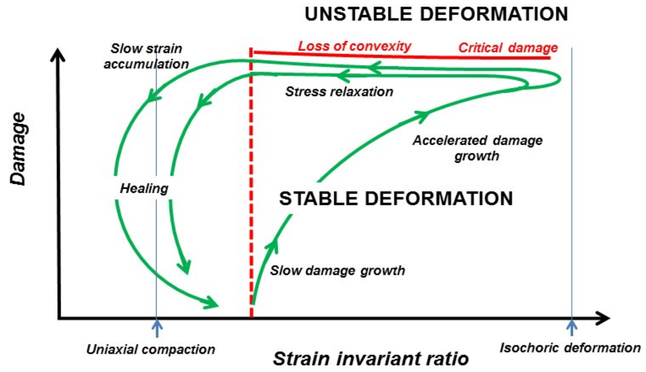


Figure 5.13. The earthquake cycle as modelled by a non-local form of the energy involving diffusion and healing of damage. From Lyakhovsky et al. (2011).

As an example of a model in which the system continuously revisits criticality we consider one developed by Lyakhovsky et al. (2008). The theory begins with the definition of the Helmholtz energy for a damaging solid where damage is defined as any process (brittle or viscous) that degrades the load bearing capacity of the material. The Helmholtz energy as defined encompasses the energy arising from the classical linear Hooke's law but is modified by the addition of an energy term that describes the opening and closing of cracks; this results in nonlinear elasticity. The form of this definition needs to take into account that the elastic moduli depend on the nature of the deformation, particularly that the elastic moduli in tension degrade more rapidly than in compression (Lockner and Byerlee, 1980). From this energy the nonlinear constitutive equation for an elastic-viscous material with cracks may be derived. A restriction imposed by the second law of thermodynamics, namely that the entropy production must always be greater or equal to zero, is used to derive a thermodynamically admissible evolution law for subsequent damage. Instability is defined by a loss in convexity of the Helmholtz energy; as we have seen this can coincide with a bifurcation where the governing equations lose ellipticity (Rudnicki and Rice, 1975) but in general the two criteria for instability do not coincide and in this instance loss of convexity precedes loss of ellipticity. Finally the post-failure evolution is modelled using the evolution laws. The result is illustrated in Figure 5.13 where the system first evolves slowly as damage begins to accumulate and then faster until criticality, defined by loss of convexity, is reached. The system then relaxes until some healing process begins (such as precipitation of quartz). The healing process reduces the damage so that the whole process repeats. Thus the system continuously cycles through criticality as a series of avalanches.

The behaviours discussed above can be summarised as follows. Many aspects of deformation can be described as first-order phase transitions. However instead of the phase changes being sharp as in classical, ideal first-order transitions the ones of interest are extended over a broader range of driving parameters (such as stress or strain) and they show hysteresis which is manifest as different behaviours under different loading conditions. These behaviours arise because the energy barriers involved (forest dislocations, regions of increased strength or elastic moduli) are large in magnitude compared to thermal fluctuations and are of relatively large spatial extent. The energy landscape consists of a numerous local minima (Figure 5.16) and the energy barriers are such that thermal fluctuations play a negligible role. The system can only move from one energy-well to another through the external driving force. This means that thermal fluctuations alone are not enough to drive the phase transition and high levels of stress or of strain are necessary. The high energy barriers have two origins: (i) initial (quenched) disorder that is inherited from a former state; these determine initial nucleation sites for the new phase; (ii) new microstructure such as fracture surfaces and dislocations which are spatially localised. This means that the response of the material to a constant driving force is a series of nucleation and collective de-pinning events expressed as discontinuous jumps, as local high strength regions are overcome and neighbouring regions take up the stress, followed by periods of quiescence when propagation of the advancing phase boundary is pinned. The next avalanche is associated with de-pinning of this boundary and this de-pinning event is expressed as an avalanche of damage events.

5.6 Emergence and pattern forming processes.

Complex systems generally show a feature called *emergence* whereby scaling phenomena approaching criticality and long range correlations together with power law probability distributions appear at a criticality. These characteristics are examples of pattern formation but there are many more including the development of fractal microstructures and/or patterns consisting of stripes (layers in three dimensions) or spots (porphyroblasts). These patterns are the result of interaction between chemical reactions, diffusion and mass transport in a fluid commonly known as reaction-diffusion-transport systems. Hydrothermal systems are particularly prone to pattern formation processes because of the nature of the chemical reaction systems that are developed. As we will see in Chapter 8, these have the following characteristics:

- The chemical reactions are almost always networked so that one chemical reaction cannot proceed without the input of products from other reactions. The outcome is that reaction products can oscillate in concentration both in time and space. The system as a whole can behave as an autocatalytic system even if no single reaction is autocatalytic.
- Most reactions are replacement reactions so that pseudomorphism is the norm rather than the exception. This means the reactions are constant volume (Figure 5.15 a) rather than constant mass as is commonly proposed. The result is that dissolution of grains and subsequent growth of new phases is strongly coupled by processes operating at grain boundaries. The outcome is oscillatory growth as growth competes with supply of nutrients. The constant volume nature of the replacement means that these reactions have some of the characteristics of continuous phase transitions. The growth process is not one of classical nucleation driven by competition between decreases in Gibbs energy and increases in surface energy followed by grain growth driven by minimisation of surface energy. The process instead is one of the development of heterogeneities as a critical point is approached; these heterogeneities coarsen as the critical point is approached with the development of power law distributions of grain size at the critical point. The microstructure is characterised by compositional fluctuations at all scales so that any one phase can be included in any other phase. One should compare Figure 5.14 (b) with Figure 5.15 (b). The contrast between the two types of microstructure is shown in Figures 5.14 (a and b). The constant volume nature of the reactions means that most are autocatalytic.
- Although the chemical reactions in the transporting fluid may well be classical abrupt transitions (this is yet to be proved), the reactions that produce the solid phases are reaction-diffusion processes and many (such as the formation of gold and arsenic at the surface of a

growing arseno-pyrite grain) occur at surfaces which are well documented as oscillatory reactions (Ertl, 2007).

- Since a number of processes may result in the deposition of gold or the development of mineral assemblages (see Figure 5.15 c and d) the distribution of various chemical elements may scale differently with different length scales. This means the distributions are multifractal.

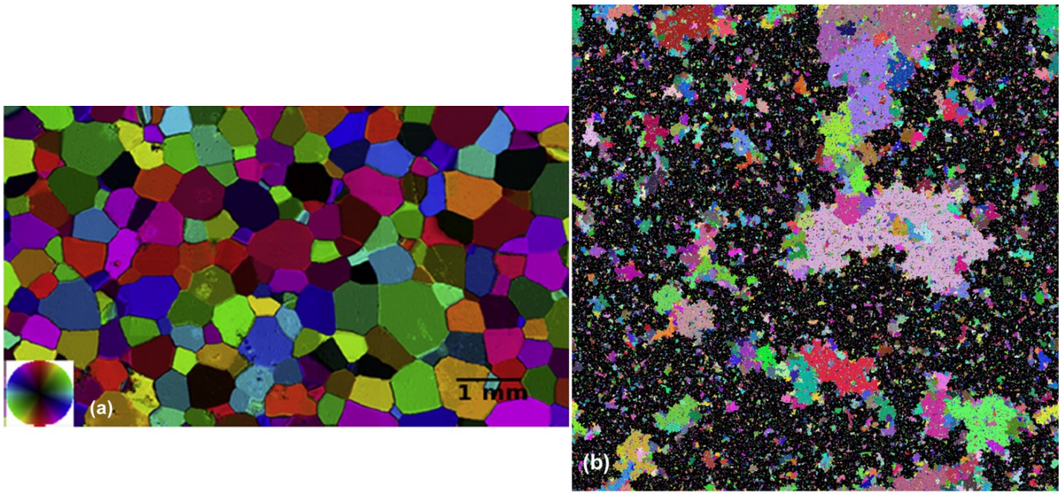
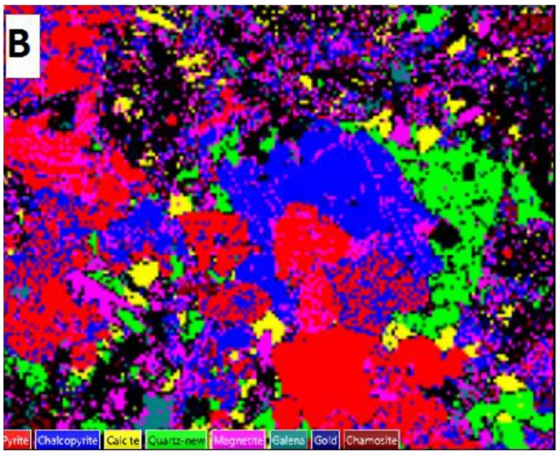


Figure 5.14. The two different types of grain growth structures. (a) Curvature driven coarsening arising from interfacial energy controlled nucleation and growth, typical of abrupt transformations. (b) Coarsening typical of continuous transformations where “nuclei” are initial fluctuations in composition and growth is due to agglomeration as criticality is approached. There are compositional fluctuations at all scales.



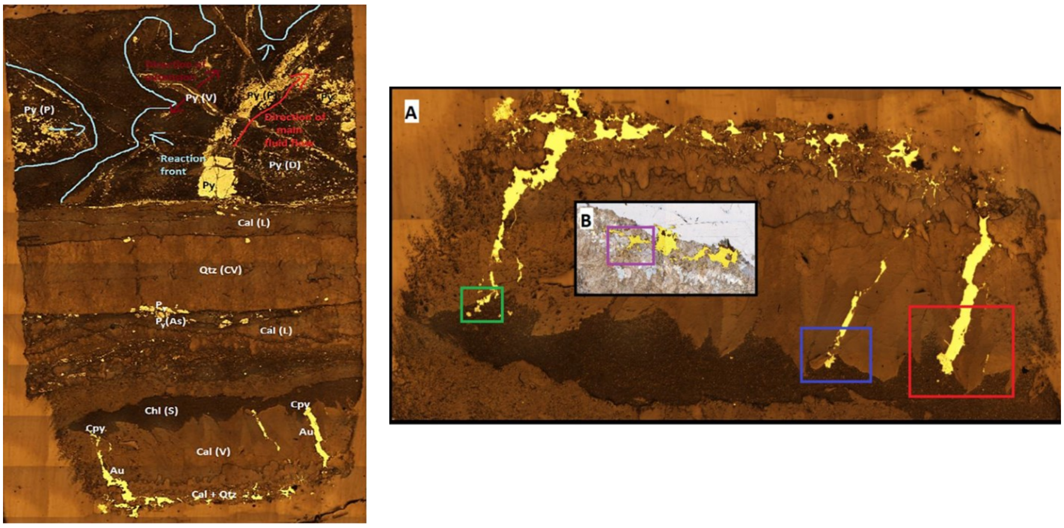


Figure 5.15. Examples of mineral microstructures in a hydrothermal gold system (Sunrise Dam in the Yilgarn of Western Australia). (a) Constant volume alteration . The sericite alteration replaces the matrix of the rock with no displacement of markers (bedding). (b) Microstructure revealed by back-scattered electron imaging. The various phases are labelled. Notice there are compositional fluctuations at all scales. Most phases include other phases except for gold. (c) Back-scattered electron map showing the wide range of alteration products. (d) Distribution of gold.

Patterns form in systems held away from equilibrium (Walgraef, 1987; Cross and Hohenberg, 1993; Cross and Greenside, 2013) and arise in some instances from the competition between two or more processes. For instance in nonlinear chemical systems (Chapter 8) patterned arrays of layers or clusters can form: diffusion tends to homogenise chemical compositions whist chemical reactions tend to localise chemical compositions. Competition between these two processes results in pattern formation. Most pattern forming processes do not involve a nucleation stage and the patterns emerge spontaneously at some stage in the evolution of the system by coarsening of heterogeneities that begin to form as criticality is approached; the coarsening scales as the critical point is approached.

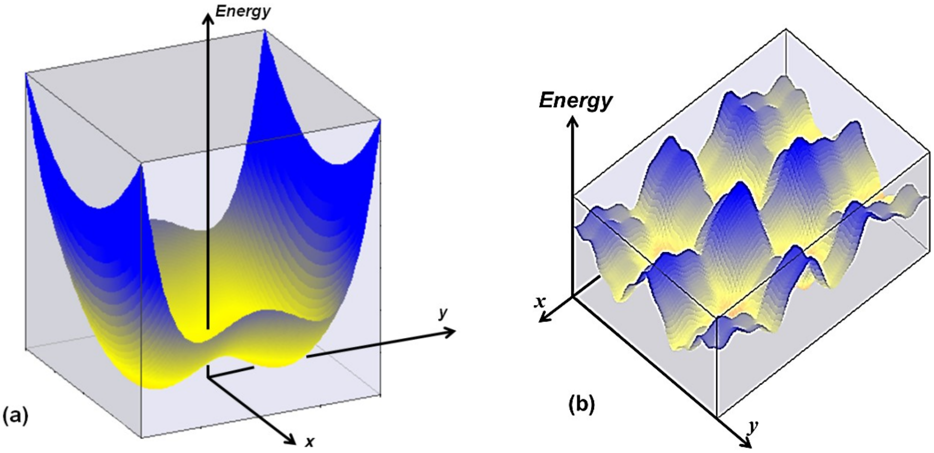


Figure 5.16. Energy configurations as a function of two variables, x and y. (a) A two-well energy potential representing two states where the energy is minimised. (b) A multi-well energy function where, as the system evolves, a number of local ststes are available to minimise the local energy function. The system evolves by jumping from one energy well to another. If the energy barriers are large compared to thermal fluctuations then *avalanche* behaviour is possible as the driving force overcomes a local barrier only to throw impediments to subsequent evolution of the system onto another nearby energy barrier.

Mathematically, pattern formation is a difficult process to treat. In the simplest of nonlinear systems the energy function has two basins as shown in Figure 5.16 (a) which means that there are two stable solutions to the equations that describe pattern formation and the resulting pattern consists of a regular array of spots or stripes. However for most cases the equations involved constitute a system of coupled nonlinear equations that may be impossible to solve analytically with current mathematical tools or sometimes the equations can be shown to have an indefinite number of solutions. The system hops from one solution to another as it evolves; each solution corresponds to a basin within a rugged energy topography such as is illustrated in Figure 5.16 (b). A common approach is to make some assumptions that hopefully are realistic physically and chemically in order to make the equations involved linear. It is then possible to perturb the system by a small amount and analyse whether the perturbed state is stable (returns to its unperturbed state) or is unstable (grows into a pattern). In nonlinear systems such a solution is only valid for the conditions where the initial linearization assumptions hold. One cannot make predictions about the pattern after these assumptions break down and commonly the system switches to another state at that stage. The initial growth rates predicted by the linear analysis (which are commonly exponential) slow down once the nonlinear effects start to dominate. Generally computer simulation is the only way to proceed but even there sensitivity to initial conditions and to the boundary conditions may lead to solutions that are not general. One should be aware of these issues in examining claims made in the literature.

Pattern forming processes and mechanisms are well understood for some small systems but are still a matter of active research in large systems with many interacting processes operating; much is still to be learnt and hydrothermal systems offer many opportunities to not only further their understanding but to advance the subject of pattern formation in large nonlinear systems in general. The approach we take is threefold:

- Study simple, small, tractable nonlinear systems with the hope that lessons learnt from such systems will guide insight into larger systems. Some motivation for this approach is that even the simplest of systems show complexity that seems to be repeated in large systems.
- Try to document the complexity in the large systems of interest (in our case, a mineralised hydrothermal system) in as much qualitative and quantitative detail as possible using tools that have proved useful in small systems.
- Develop models for the system involved based on the physics and chemistry of the processes involved in an attempt to reproduce both the qualitative and quantitative observations.

These kinds of studies have only recently begun for hydrothermal systems but considerable insight is already available as we will summarise in Chapters 10 and 11.

5.7. Criticality in crustal plumbing systems.

As an example of power law distributions in critical systems we present in Figure 5.17 the distribution of Darcy velocity in the percolation networks modelled in Section 3.6 and particularly in Figure 3.30. Criticality in this system corresponds to a probability of fracture, $p = 0.59$. In Figure 5.17 we show probability distributions of the Darcy velocity, v, as a plot of the logarithm of the number of sites, N(v) with velocity, v, against log(v) for $p = 0.5$ and for $p = 0.6$. The distributions follow a power law relation of the form $N(v) = \alpha v^{-0.35}$ where α is a constant for a given p until exponential decay (very high slopes) ultimately sets in at high values of v. This type of relationship is typical of many critical systems in the vicinity of criticality.

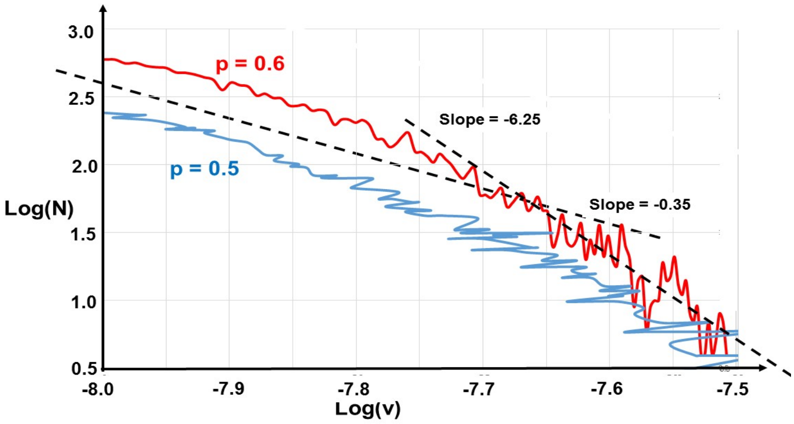


Figure 5.17. Power law relationships near criticality for the Darcy velocities, v, in the percolation plots of Figure 3.30. N(v) is the number of sites with velocity, v. p is the probability of fractiure at a particular site.

5.8. Summary.

In nonlinear systems we are interested in situations where there is a system-wide change in behaviour of the system. This change in behaviour is called a *phase transition* and examples in hydrothermal systems are the change from unaltered to altered, undeformed to brecciated, homogeneous to veined and un-mineralised to mineralised.

Transitions result from two processes:

- An evolution of the Gibbs or Helmholtz energies from *convex* to *non-convex*; this type of phase transition can be of two types: *abrupt* (or first order) or *continuous* (or second order). These transitions are said to result from a *loss of convexity*. The loss of convexity in a continuous transition is called a *critical point*; it is characterised by the scaling of characteristic properties of the system as criticality is approached (in other words organisation of the system begins as criticality is approached). At criticality long range correlations emerge with power law probability distributions.
- An evolution of a control parameter leads to a *bifurcation* which is an expression of a change in the character of the underlying mathematical equations; the character of the equations changes from elliptic to hyperbolic. This transition is referred to as a *loss in ellipticity*. Physically this stems from the competition between two (or more) processes reaching a state where system behaviour can follow one of two possible paths. In mechanical systems a bifurcation commonly is expressed as a shear localisation resulting from the plastic hardening reaching a state where competition with elastic loading means that the system can switch

from homogeneous deformation to localised deformation. In chemical systems that evolve according to reaction-diffusion-transport equations, bifurcation marks loss of stability and the development of spatio-temporal patterning. Bifurcations can be of three broad classes: *safe*, *explosive* or *dangerous*.

Abrupt transitions are characterised by an exponential change in some characteristic parameters (such as the concentration of a metastable phase) as the transition point is approached. At the transition point there is a power law distribution of characteristic parameters. The growth of the new phase takes place by a nucleation and growth process, the time dependency of growth depends on the detail of the processes assisting growth. If R is the grain size for instance then $R \sim t^{1/2}$, $R \sim t^{1/3}$, or $R \sim t^{1/4}$ depending on whether the grain growth process is controlled by diffusion through a fluid, surface diffusion or bulk diffusion.

Continuous transitions are characterised by a power law dependence on the distance from the critical point of characteristic parameters (such as density, grain size, lamella width) as the critical point is approached with a singularity occurring at the critical point and power laws for the distribution of characteristic parameters at criticality (which means there is no characteristic length scale).

In principle the two types of transitions, phase transitions and bifurcations, are distinct phenomena and in some systems phase transitions occur before bifurcations and *vice versa*. In some systems both types of transitions can occur together. Thus many authors propose that continuous transitions are equivalent to safe bifurcations whereas abrupt transitions are equivalent to explosive bifurcations. This can only be true for some systems and in general the two phenomena are distinct.

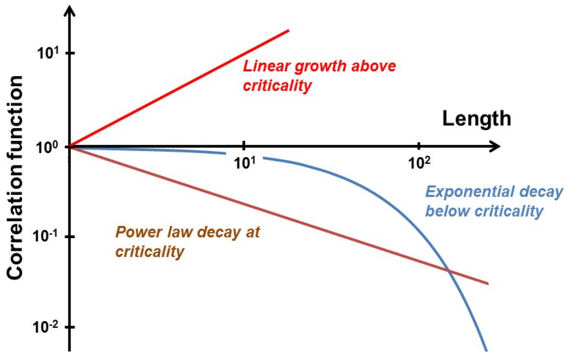
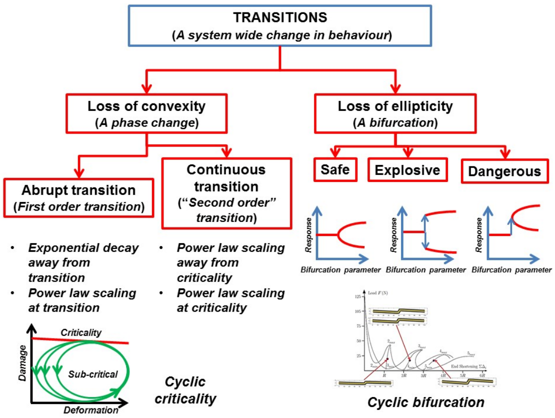


Figure 5.18. Spatial scaling of the correlation function below criticality (blue), at criticality (brown) and above criticality (red).

In many systems the control parameter evolves so that the system evolves from a sub-critical state (with exponential decay of characteristic features) through criticality (with power law distributions of characteristic features) to super-critical states where characteristic features scale in a linear manner with distance from criticality. As an example the behaviour of the correlation function is shown in Figure 5.18. Exponential decay results from short range interactions whereas power law decay results from long range interactions, ideally on the scale of the system as a whole.

However in some systems the control parameter is influenced by the state of the system (that is, feedback interactions exist) and evolves in such a way that the system continuously cycles through a critical state. This means, for large systems or long times, the system on average is critical. This situation is referred to as *self-organised criticality* by many authors. Since it is possible for some systems to cycle through successive bifurcations (*snakes and ladders* behaviour is an example, Knobloch, 2008) whilst others could cycle through critical state → bifurcation → critical state, one could call the SOC example *repetitive criticality*. The other two modes of evolution mentioned above then become systems characterised by *repetitive bifurcation* and *repetitive criticality/bifurcation*. The type of repetitive behaviour depends on the feedback processes operating between evolution of the system and the nature of the control parameter and can only be distinguished with careful quantitative analysis. These system behaviours are summarised in Table 5.3.

Table 5.3. Division of transitions into phase changes and bifurcations.



Lastly, the microstructures that develop from abrupt (non-critical) phase transitions and from continuous (critical) phase transitions are quite different. Abrupt transitions lead to distinct phases with grain size distributions controlled by competition between minimising interfacial energies and other processes that decrease grain size (Zollner and Streitenberger, 2008). Long range correlations do not develop. By contrast continuous phase transitions lead to irregular grain shapes with heterogeneities at all scales and long range correlations. The grain size distribution is multifractal.

Recommended reading.