Chapter 10
Fast/slow Dynamical Systems

In previous chapters we employed perturbation methods to study problems in differential equations where the solution of the leading order problem could be obtained in a simple explicit form. For problems where the leading order solution cannot be obtained in a simple form, a different approach is needed. Here we show that ideas from phase plane analysis (Chap. 1) can be used to circumvent these difficulties and allow us to apply boundary layer methods (Chap. 7) to separate problems into dynamics occurring at different scales.

The fundamental principles for formulating rate equations given in Chap. 1 are universally applicable for constructing models. But when the number of equations in the resulting system is large or the leading order problem for $\varepsilon = 0$ is nonlinear, then some of the direct approaches that we have seen in previous chapters become cumbersome and may not be useful.

Similarly, Chap. 9 introduced approaches based on perturbation methods to estimate the behaviour of some models yielding oscillatory behaviours. But those methods were limited to *weakly* nonlinear problems, where the leading order solution satisfied a linear oscillator equation and could be calculated explicitly in terms of sines and cosines. For some more general nonlinear problems, we will show that properties of the system can be determined without the need for a closed-form solution.

The common structure for problems that we will investigate in this chapter is that of singularly-perturbed dynamical systems. In Chap. 7, we've learned that singularly perturbed differential equations exhibit separation of spatial scales, having rapid variations in boundary layers in contrast to slowly-varying outer solutions. Likewise in Chap. 9, a separation of time-scales occurred between the oscillations on the fast time scale and evolution of the amplitude functions on slow scales. Extending this approach to more general dynamical systems, we seek to decompose each problem into two sub-systems:

- *The slow system*: the problem in terms of the original ("slow-time") variable, whose solution will be treated analogously to the outer solution in a boundary layer problem.

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- *The fast system*: a rescaling of the system describing rapid evolution occurring over shorter times, analogous to the inner solution of a boundary layer problem.

The solution of each sub-system will be sought in the form of a regular perturbation expansion. For singularly-perturbed problems, the sub-systems will have simpler structures than the full problem and allow for the slow- and fast-dynamics to potentially be characterised in terms of reduced phase line or phase plane dynamics.

We will study two problems that could be considered directly in terms of a standard phase plane analysis, but through the use of perturbation theory (that is also applicable to higher order systems), we will show that the underlying dynamics can be separated into more convenient forms.

10.1 Strongly-Nonlinear Oscillators: The van der Pol Equation

For oscillatory systems where the leading problem for $\varepsilon \to 0$ does not yield the harmonic oscillator equation, $x_0''(t) + x_0(t) = 0$, the approaches from Chap. 9 cannot be applied in a straightforward manner. As an example of a "*strongly nonlinear*" oscillator, we will show how to construct solutions of the *van der Pol oscillator*,

$$\varepsilon \frac{d^2x}{dt^2} + (x^2 - 1)\frac{dx}{dt} + x = 0 \qquad \text{for } \varepsilon \to 0. \tag{10.1}$$

This equation is similar to the weakly-nonlinear damped oscillator (9.33), but here the first-order damping term is part of the leading order equation while the second derivative term is a singular perturbation.[1] Since the perturbation parameter here multiplies the highest order derivative, this type of problem could be called a "singularly perturbed oscillator" but the more common name is a *relaxation oscillator*.

We begin by re-writing (10.1) in terms of a convenient formulation for a phase plane analysis but will use a different choice of intermediate variable $y(t)$ than the standard velocity (1.37). Notice that the first two terms in (10.1) can be written as a total derivative,

$$\frac{d}{dt}\left(\varepsilon \frac{dx}{dt} + \tfrac{1}{3}x^3 - x\right) + x = 0.$$

Defining the expression in parentheses as $y = \varepsilon x' + \frac{1}{3}x^3 - x$, we obtain an autonomous system for $(x(t), y(t))$,

$$\varepsilon \frac{dx}{dt} = y + x - \tfrac{1}{3}x^3, \qquad \frac{dy}{dt} = -x, \tag{10.2}$$

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[1] Attempting to put this equation in the form (9.2) fails because dividing by ε suggests a very fast oscillation, $\omega_0 = \varepsilon^{-1/2} \to \infty$, and a large ($O(\varepsilon^{-1}) \to \infty$) rather than small perturbation term.

which is called the *Liénard transformation* of the van der Pol equation. The singularly-perturbed nature of this system is clear: for $\varepsilon = 0$, the ODE for $x(t)$ reduces to an algebraic relation.

We begin by determining the outer ("slow") solution using regular perturbation expansions for both x, y:

$$x(t) = x_0(t) + \varepsilon x_1(t) + O(\varepsilon^2), \qquad y(t) = y_0(t) + \varepsilon y_1(t) + O(\varepsilon^2).$$

Collecting the $O(1)$ terms in the expansions of (10.2), we obtain the leading order slow system,

$$0 = y_0 + x_0 - \tfrac{1}{3}x_0^3, \qquad \frac{dy_0}{dt} = -x_0. \tag{10.3}$$

The differential equation for $y_0(t)$ allows us to qualitatively describe the dynamics of the solution in terms of vertical motion in the phase plane as

$$y_0(t) \quad \text{is} \begin{cases} \text{decreasing for } x_0 > 0, \\ \text{increasing for } x_0 < 0; \end{cases} \tag{10.4a}$$

hence the y_0-axis is the y-nullcline curve (see Sect. 1.5.1) for both the full problem and the slow system. The remaining equation in (10.3) restricts the slow-time solution to evolve only on the curve

$$y_0(x_0) = \tfrac{1}{3}x_0^3 - x_0 \equiv S(x_0), \tag{10.4b}$$

which is called the *slow manifold* (or "slow solution curve") and is shown in Fig. 10.1.

Restricting the solution to stay on the slow manifold while following the evolution described by (10.4a) suggests that starting from any $x_0 < 0$ will drive the solution upward to approach the local maximum of the curve at $y_0(-1) = 2/3$, while the dynamics in the right half plane, with $x_0 > 0$ will force solutions to evolve toward the local minimum at $y_0(1) = -2/3$. At those critical points (extrema), the vertical motion still follows (10.4a) even though there is no obvious place to go on the slow

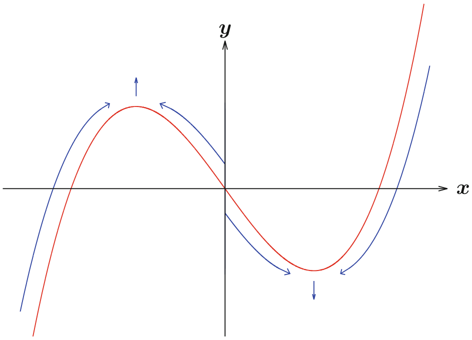

Fig. 10.1 *Arrows* indicating dynamics of the leading order solution on the slow manifold (10.4b) and at the two critical points of the *curve*

manifold. The solution therefore gets *pushed off* the slow manifold[2]; everything off the slow manifold in the phase plane is part of the *fast problem*, to which we now turn our attention.

Following the analysis in Chaps. 6 and 7, in order to find singular solutions, we rescale the original system in terms of new variables. To determine the fast variables, we substitute the general scalings

$$T = \frac{t - t_*}{\varepsilon^\alpha}, \qquad x = \varepsilon^\beta X(T), \qquad y = \varepsilon^\gamma Y(T), \tag{10.5}$$

into (10.2) where the scaling exponents α, β, γ and the time t_* when the fast dynamics occur are to be determined. For this problem, it can be shown that x, y are always $O(1)$, so we take $\beta = \gamma = 0$ and determine the value for $\alpha(\geq 0)$ from dominant balance in

$$\varepsilon^{1-\alpha}\frac{dX}{dT} = Y + X - \tfrac{1}{3}X^3, \qquad \varepsilon^{-\alpha}\frac{dY}{dT} = -X.$$

In applying the method of dominant balance to systems of equations, distinguished limits will typically yield a balance in one equation at a time, while the other equations yield sub-dominant contributions, where the rate of change will be $o(1)$. The distinguished limit $\alpha = 0$ balances the terms in the second equation and reproduces the original slow system we have already considered, (10.2). The choice $\alpha = 1$ balances all of the terms in the first equation,

$$\frac{dX}{dT} = Y + X - \tfrac{1}{3}X^3, \qquad \frac{dY}{dT} = -\varepsilon X, \tag{10.6}$$

where we have multiplied the second equation by ε^α.

Seeking the fast solutions as regular expansions,

$$X(T) = X_0(T) + \varepsilon X_1(T) + O(\varepsilon^2), \qquad Y(T) = Y_0(T) + \varepsilon Y_1(T) + O(\varepsilon^2),$$

yields the leading order fast system,

$$\frac{dX_0}{dT} = Y_0 + X_0 - \tfrac{1}{3}X_0^3, \qquad \frac{dY_0}{dT} = 0. \tag{10.7}$$

The second equation shows that the dynamics in the fast system (everywhere in the phase plane away from the slow manifold) must have $Y_0(T) \equiv$ constant, i.e. only horizontal motion is admissible. With this in mind, the first equation can be interpreted as describing motion on a phase-line for $X_0(T)$,

$$\frac{dX_0}{dT} = Y_0 - S(X_0), \tag{10.8}$$

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[2] At which point, the solution is no longer described by the dynamics of the slow system.

where the value of Y_0 selects a "slice" through the slow-manifold analogous to (1.29) from Chap. 1. The equilibrium points of (10.8) are given by the solutions of $S(X_0) = Y_0$ with their stability being determined by the sign of $-S'(X_0)$, while all other values for X_0 give monotonic increasing or decreasing solutions.

In summary, for the slow system, we have identified the slow manifold and described how the dynamics on the slow manifold approach the critical points. Taking those as departure points into the fast system, the subsequent motion is given by the rapid evolution of x on horizontal lines that terminate at points of intersection with the slow curve. This qualitative description allows us to sketch the form of trajectories starting from any point in the (x, y) phase plane and identify the four-stage structure (and global stability) of the stable finite-amplitude *limit cycle* solution, see Figs. 10.2 and 10.3. The general features of the limit cycle (maximum, minimum values and period) can be obtained from these results (see Exercise 10.1). The fast-time dynamics can be asymptotically matched to outer solutions (slow solutions), and so the fast-dynamics act as "interior" boundary layers (in the terminology of Chap. 7).

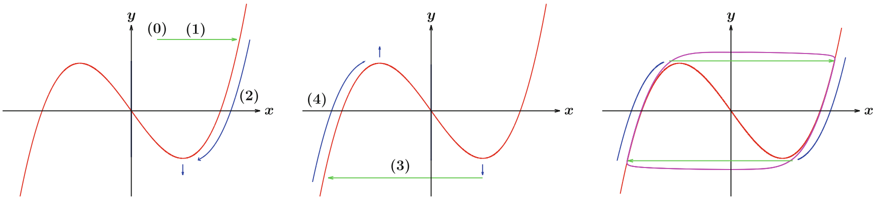
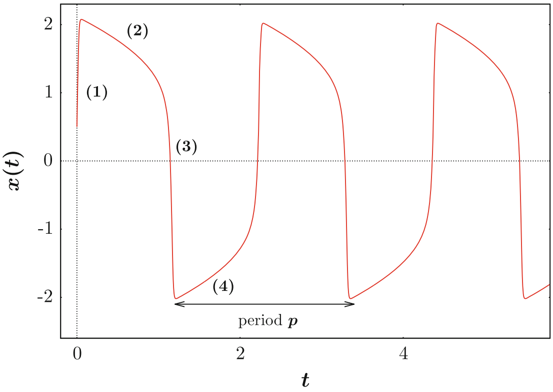


Fig. 10.2 Starting from general initial conditions not on the slow manifold, there will first be a rapid horizontal transition or "jump" *1* to a stable branch of the slow manifold followed by slow evolution down that branch *2* to the equilibrium point. Dropping off the minimum yields another fast jump *3* across to the other stable branch of the slow manifold, where slow dynamics drive the solution upwards *4* to the maximum and on to another fast jump back across to the previous stable branch of the slow manifold. The resulting (periodic) dynamics correspond to an attracting limit cycle

Fig. 10.3 Sketch of the time-profile illustrating the four stages in the van der Pol limit cycle



10.2 Complex Chemical Reactions: The Michaelis-Menten Model

The reactions described in Sect. 1.2 can be said to be "what you see is what you get" elementary reactions if the rate equations obtained from direct applications of the the law of mass action predicts the rates as would be observed in experimental studies of the systems. However, for general reactions, collisions of three or more molecules almost never happen exactly simultaneously (only single-molecule decay or binary collisions typically occur as elementary steps). The term *non-elementary reactions* describes the overall relation between reactants and products, but with the molecular collisions and mass action kinetics involved actually occurring in many "hidden" intermediate sub-stages. For example, a non-elementary version of (1.14a) could be

$$n\,A + m\,B \to (???) \to (???) \to (???) \to p\,C + q\,D.$$

The temporary products from intermediate reactions are called *complexes* and are often unstable compounds that exist only briefly.

To obtain the overall rate of creation of products, we need to analyse the full system with all intermediate stages expanded out as elementary reactions. Part of the very difficult work of chemists and bio-chemists is to determine all of the intermediate reactions. If all of the intermediate reactions are known, then we may have a very complicated system of rate ODEs. Our goal is to try to condense the system down to just the overall reaction

$$\text{reactants} \rightsquigarrow \text{products}$$

and to determine the effective rate equation for the products. The theory of dynamical systems can be applied to accomplish this for many chemical reaction systems. Given a complete system of reactions and initial conditions, we illustrate through an example how to obtain a simple model for the rate equations of the products.

A simple version of an enzyme-mediated chemical reaction process is given by the system,

$$S + E \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C \overset{k_3}{\to} P + E, \tag{10.9}$$

where S is the "substrate" reactant and P is the concentration of the desired product. An enzyme (or catalyst) is a compound whose special property is that it allows for intermediate reaction steps that lead to the overall reaction, in this case

$$S \to P, \tag{10.10}$$

or allow it proceed more rapidly than without the enzyme; in some cases this direct transformation might not be possible at all without the enzyme.

Let E be the concentration of the enzyme, and C is the intermediate "complex" of SE bound together. The enzyme is typically a complicated and expensive compound, but notably it is not actually consumed by (10.9). Consequently, the enzyme may be given in a small initial concentration E_0. The complex C is an unstable temporary state and none would be present before the reaction starts. We will assume that the production process begins with no product, and a large initial supply of reactant, S_0, all to be converted into P. Assuming the reaction rate constants k_1, k_2, k_3 are known finite values, our goal is to determine the rate of production for P and how it can be represented in simplest form.

Beginning by expanding (10.9) into its full set of elementary reactions,

$$S + E \xrightarrow{k_1} C \qquad S + E \xleftarrow{k_2} C \qquad C \xrightarrow{k_3} P + E, \tag{10.11}$$

the law of mass action yields the rate equations for consumption/production of each chemical species in the dimensional form

$$\begin{aligned} \frac{d\mathsf{P}}{d\mathsf{T}} &= \mathsf{k}_3\mathsf{C}, & \frac{d\mathsf{C}}{d\mathsf{T}} &= \mathsf{k}_1\mathsf{S}\mathsf{E} - \mathsf{k}_2\mathsf{C} - \mathsf{k}_3\mathsf{C}, \\ \frac{d\mathsf{S}}{d\mathsf{T}} &= -\mathsf{k}_1\mathsf{S}\mathsf{E} + \mathsf{k}_2\mathsf{C}, & \frac{d\mathsf{E}}{d\mathsf{T}} &= -\mathsf{k}_1\mathsf{S}\mathsf{E} + \mathsf{k}_2\mathsf{C} + \mathsf{k}_3\mathsf{C}, \end{aligned} \tag{10.12a}$$

subject to initial conditions at $t = 0$,

$$\mathsf{S}(0) = \mathsf{S}_0, \qquad \mathsf{E}(0) = \mathsf{E}_0, \qquad \mathsf{C}(0) = 0, \qquad \mathsf{P}(0) = 0. \tag{10.12b}$$

We now nondimensionalize system (10.12a, 10.12b). Given the one-to-one correspondence between S and P and between E and C as reactants/products in (10.11), we scale these pairs by the respective initial concentrations

$$\begin{gathered} \mathsf{S}(\mathsf{T}) = \mathsf{S}_0 s(t), \qquad \mathsf{P}(\mathsf{T}) = \mathsf{S}_0 p(t), \\ \mathsf{E}(\mathsf{T}) = \mathsf{E}_0 e(t), \qquad \mathsf{C}(\mathsf{T}) = \mathsf{E}_0 c(t), \qquad \mathsf{T} = \mathrm{T}t. \end{gathered} \tag{10.13}$$

We will go on to select the timescale T later below. Through these scalings, the nondimensional concentrations are all normalised such that

$$0 \le \{s(t), p(t), e(t), c(t)\} \le 1.$$

Our previous intuition related to the transformation of enzyme to complex molecules, $E \rightleftharpoons C$, can be made concrete by noting that the total amount of the two substances is conserved for all times, following directly from (10.12a),

$$\frac{d}{d\mathsf{T}}(\mathsf{C} + \mathsf{E}) = 0 \implies \mathsf{C}(\mathsf{T}) + \mathsf{E}(\mathsf{T}) = \mathsf{E}_0,$$

so that $c + e = 1$. This allows us to use $e = 1 - c$ to eliminate the enzyme from the system, leaving the problem in terms of s, c, p.

We take the initial amount of substrate to be finite, $\mathsf{S}_0 = O(1)$, and assume that we begin with a relatively small amount of enzyme, $\mathsf{E}_0 \ll \mathsf{S}_0$. We now select the timescale T in order to make the consumption rate $ds/dt = O(1)$. This choice yields $\mathrm{T} = 1/(\mathsf{k}_1 \mathsf{E}_0)$. The resulting scaled system is therefore given by

$$\begin{aligned} \frac{ds}{dt} &= -s(1-c) + \lambda c, \qquad && s(0) = 1, \\ \varepsilon \frac{dc}{dt} &= s(1-c) - \mu c, && c(0) = 0, \\ \frac{dp}{dt} &= (\mu - \lambda)c, && p(0) = 0, \end{aligned} \tag{10.14}$$

where we have relabelled dimensionless combinations of parameters as

$$\varepsilon = \frac{\mathsf{E}_0}{\mathsf{S}_0} \ll 1 \qquad \lambda = \frac{\mathsf{k}_2}{\mathsf{k}_1 \mathsf{S}_0} = O(1) \qquad \mu = \frac{\mathsf{k}_2 + \mathsf{k}_3}{\mathsf{k}_1 \mathsf{S}_0} = O(1). \tag{10.15}$$

We will consider the limit of a very small amount of enzyme in the system ($\varepsilon \to 0$) for our perturbation analysis. Noting that the equations for s, c are independent of p, we first solve for the s, c system and then use the results to determine p from the final equation in (10.14).

Since (10.14) is a singularly perturbed system for $\varepsilon \to 0$, we expect a separation between fast and slow time scales. Beginning with the slow system, we consider regular expansions for the solutions, $s = s_0(t) + O(\varepsilon)$, $c = c_0(t) + O(\varepsilon)$. Substituting these into (10.14) yields the leading order slow system,

$$\frac{ds_0}{dt} = -s_0(1-c_0) + \lambda c_0, \qquad 0 = s_0(1-c_0) - \mu c_0, \tag{10.16}$$

with the second equation giving an algebraic relationship between the complex and substrate concentrations,

$$s_0(c_0) = \frac{\mu c_0}{1-c_0}; \tag{10.17}$$

this is the slow manifold for this problem.

We note that our initial conditions, $c(t=0) = 0$, $s(t=0) = 1$ do not lie on the slow manifold and hence there must be a brief *initial layer* at $t_* = 0$, governed by the dynamics of the fast system, that describes the transition from the initial conditions to the slow manifold. To determine the form of the fast system, we rescale the variables as

$$s = S(T), \qquad c = C(T), \qquad T = \frac{t}{\varepsilon^\alpha},$$

yielding

$$\varepsilon^{-\alpha} \frac{dS}{dT} = -S(1-C) + \lambda C, \qquad \varepsilon^{1-\alpha} \frac{dC}{dT} = S(1-C) - \mu C.$$

The distinguished limit for the fast system is found to occur when $\alpha = 1$ and the leading order fast system is then given by

$$\frac{dS_0}{dT} = 0, \qquad \frac{dC_0}{dT} = S_0(1 - C_0) - \mu C_0, \tag{10.18}$$

with initial conditions $S_0(0) = 1$ and $C_0(0) = 0$. Consequently there is no change to the substrate concentration in the initial layer at leading order, and it remains at its initial value, $S_0(T) \equiv 1$. For completeness, we could determine $C_0(T)$ from this system, but bearing in mind that our final goal is to determine $p(t)$, we only actually need to find $s(t)$ as we can replace $c(t)$ in terms of $s(t)$ (at leading order) in (10.14) using the slow manifold (10.17). Asymptotic matching of the fast and slow solutions for s yields the initial conditions for the slow solution,

$$\lim_{T\to\infty} S_0(T) = 1 = \lim_{t\to 0} s_0(t).$$

Hence, while the initial layer has a dramatic effect on the concentration of the complex, it essentially leaves the initial condition on s from (10.14) unchanged. The initial layer is effectively a boundary layer with respect to time for the initial value problem for c in (10.14). Figure 10.4 shows a comparison of the numerical solution of (10.14) against the leading order fast/slow dynamics (the slow manifold being described by (10.17)).

Substituting (10.17) into (10.14), we get the slow system,

$$\frac{ds_0}{dt} = -\frac{\mu - \lambda}{\mu + s_0} s_0, \qquad \frac{dp_0}{dt} = \frac{\mu - \lambda}{\mu + s_0} s_0, \tag{10.19}$$

and we can finally confirm our expectation that the total of the substrate and product is conserved, $d(s_0 + p_0)/dt = 0$. Using the initial conditions, we have effectively reduced the original problem to solving a single first order ODE for $s_0(t)$, with $p_0(t)$ then being given by $p_0(t) = 1 - s_0(t)$. This effective nonlinear rate law is called the *Michaelis-Menten* law and is used extensively in the modelling of biochemical systems.

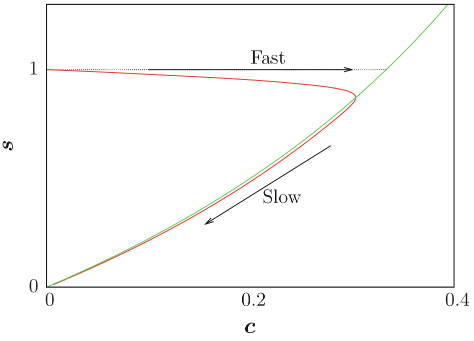


Fig. 10.4 The cs phase plane showing the slow manifold *curve* (10.17) and a numerical solution of the full system (10.14) for $\varepsilon = 1/5$ starting from initial condition $(c, s) = (0, 1)$

10.3 Further Directions

More extensive presentations of dynamical systems are given in many texts, both from more theoretical [43, 70], and more applied standpoints [54, 94]. Many books illustrate in detail the use of perturbation methods for studying dynamical systems [47, 54, 56, 73, 102], with the van der Pol oscillator being a classic example. Modelling and applications of chemical kinetic systems are presented more thoroughly in [37, 49, 57, 74]. Some alternative limiting cases of the enzyme kinetics system are explored in [87, 90].

10.4 Exercises

10.1 Consider the van der Pol equation for $x(t)$ with $0 < \varepsilon \ll 1$,

$$\varepsilon \frac{d^2x}{dt^2} + (3x^2 - 6x - 9)\frac{dx}{dt} + 4x = 0.$$

(a) Determine $f(x)$ so that this equation can be written as a Liénard phase plane system in the form

$$\varepsilon \frac{dx}{dt} = f(x) + 4y, \qquad \frac{dy}{dt} = -x.$$

(b) For fixed $\varepsilon > 0$, find the equilibrium point(s) in the phase plane, find their eigenvalues, and classify their linear stability.

(c) Use the expansions $x(t) = x_0(t) + \varepsilon x_1(t) + O(\varepsilon^2)$, $y(t) = y_0(t) + \varepsilon y_1(t) + O(\varepsilon^2)$, to determine the equations for the leading order slow solution. Sketch the slow manifold, indicate the direction of motion on each part, and identify the two attracting points on the curve.

(d) Use the expansions $x(t) = X_0(T) + \varepsilon X_1(T) + O(\varepsilon^2)$, $y(t) = Y_0(T) + \varepsilon Y_1(T) + O(\varepsilon^2)$ with $T = t/\varepsilon$ to obtain the equations for the leading order fast solution.

(e) Use the phase plane to determine the maximum and minimum values of $x(t)$ during an oscillation, see Fig. 10.2. Sketch $x(t)$ as a function of time, see Fig. 10.3.

(f) Using the time required for the slow motions in (c) (neglecting the short times for the fast solutions (d)), determine the leading order estimate for the period P of oscillation of the limit cycle.
Hint: Find the time spent moving along each of the slow curves by obtaining an equation $dx_0/dt = g(x_0)$ from (c) and then separate variables to write

$$\frac{dx_0}{dt} = g(x_0) \implies P = \int_{t_{\text{start}}}^{t_{\text{end}}} dt = \int_{x_{\text{start}}}^{x_{\text{end}}} \frac{dx}{g(x)}$$

and finally integrate over the ranges in x that are appropriate to each of the two slow segments and adding together those two times.

10.2 We now consider different limits for a dynamical system describing a chemical reaction problem in terms of three variables, see (4.50). Consider the limit $\varepsilon \to 0$ for each of the following cases,

(a) For the system

$$\begin{aligned} \frac{dx}{dt} &= 2 - y, & x(0) &= 1, \\ \frac{dy}{dt} &= x - z, & y(0) &= 3, \\ \varepsilon\frac{dz}{dt} &= y - y^2 + \tfrac{1}{3}y^3 - z, & z(0) &= 0. \end{aligned} \tag{10.20}$$

Identify the surface $z = S(x, y)$ that defines the slow manifold. Find the equilibrium point of the leading order slow phase plane system and show that it is asymptotically stable for $t \to \infty$. Also determine the form of the initial layer that describes the transition from the initial conditions to the slow manifold.

(b) For the system

$$\begin{aligned} \frac{dx}{dt} &= 2 - y, & x(0) &= 0, \\ \varepsilon\frac{dy}{dt} &= x - z, & y(0) &= 3, \\ \frac{dz}{dt} &= y - y^2 + \tfrac{1}{3}y^3 - z, & z(0) &= 1. \end{aligned} \tag{10.21}$$

Show that the slow manifold reduces to a curve that could be written in parametric form as $x = x(z), y = y(z), z = z$. Determine the asymptotic solution for $t \to \infty$. Also determine the form of the initial layer that describes the transition from the initial conditions to the slow manifold.

10.3 Consider the problem of forming a "tri-mer" (a three segment polymer molecule) from three mono-mer molecules,

$$3A \to A_3.$$

This is an example of polymerisation. It is a non-elementary reaction and takes place via intermediate stages. Call the tri-mer "C" and the di-mer (A_2) "B". Suppose that the full reaction mechanism is given by

$$A + A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \qquad A + B \xrightarrow{k_3} C$$

(a) Write the dimensional rate equations.
(b) Nondimensionalize using the scalings

$$\mathsf{A}(\mathsf{T}) = \mathsf{A}_0 a(t) \qquad \mathsf{B}(\mathsf{T}) = \mathsf{B}_0 b(t) \qquad \mathsf{C}(\mathsf{T}) = \mathsf{A}_0 c(t) \qquad \mathsf{T} = \mathrm{T}t$$

where A_0 is the initial concentration.
(c) Let $\mathrm{T} = 1/(\mathsf{k}_1 \mathsf{A}_0)$ and assume that $\varepsilon = \mathsf{B}_0/\mathsf{A}_0 \to 0$.
Identify the other dimensionless parameters (call them Π_1, Π_2) and state what asymptotic relations on the rate constants k_n must hold if we assume that only the $\varepsilon db/dt$ terms vanishes from the leading order slow system.
Hint: Normalise the coefficient of the $+a^2$ term.
(d) Find the leading order slow manifold and write the dimensional equations for the long-term rate of production, and hence find $\mathsf{G}(\mathsf{A})$ and $\mathsf{F}(\mathsf{A})$ in

$$\frac{d\mathsf{A}}{d\mathsf{T}} = -\mathsf{G}(\mathsf{A}), \qquad \frac{d\mathsf{C}}{d\mathsf{T}} = \mathsf{F}(\mathsf{A}).$$

10.4 Consider the system of chemical reactions

$$A + X \xrightarrow{k_1} Y \qquad A + Y \xrightarrow{k_2} 2X \qquad A \xrightarrow{k_3} Y \qquad 2Y \xrightarrow{k_4} P$$

where the concentration of A is kept constant and k_1, k_2, k_3, k_4 are given.

(a) Write the rate equations for $x(t)$ and $y(t)$.
(b) Nondimensionalize using $\mathsf{T} = \mathrm{T}t$, $\mathsf{X} = \mathrm{X}x$, $\mathsf{Y} = \mathrm{Y}y$. Let $\mathrm{T} = 1/(\mathsf{k}_1\mathsf{A})$. Determine X and Y so that: (1) all of the terms in the dx/dt equation and (2) the y^2 term in the dy/dt equation are normalised.
(c) Determine the remaining independent dimensionless parameters (call them α, β) and write the nondimensionalized equations.
(d) In terms of α, β, determine the concentrations x, y for the positive equilibrium solution.

10.5 In chemistry, a widely-used short-cut avoiding the full scaling and slow/fast perturbation analysis is to jump to the leading order slow equations using the assumption that the rate of production of all intermediates equilibrate (i.e. reduce to steady algebraic relations, like $\varepsilon \frac{dc}{dt} = 0$); this is called the *Quasi-Steady-State Assumption* (QSSA).
Use the QSSA approach to consider the overall reaction for the formation of hydrogen-bromide: $H_2 + Br_2 \to 2HBr$. The reaction takes place through several steps:

$$\mathrm{Br}_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\mathrm{Br} \qquad \mathrm{Br} + \mathrm{H}_2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{H} + \mathrm{HBr} \qquad \mathrm{H} + \mathrm{Br}_2 \xrightarrow{k_5} \mathrm{HBr} + \mathrm{Br}$$

Consider the atomic forms H and Br to be unstable intermediates (similar to complexes being unstable intermediates). Apply the QSSA to obtain the dimensional rate law for the production of HBr (written here using the chemistry-notation of [X] being the concentration of chemical X) [6],

$$\frac{d[\mathrm{HBr}]}{d\mathsf{T}} = \frac{\alpha[\mathrm{H}_2][\mathrm{Br}_2]^{3/2}}{[\mathrm{Br}_2] + \beta[\mathrm{HBr}]}$$

Find α, β. Hint: Write $A = [\mathrm{H}_2]$, $B = [\mathrm{Br}_2]$, $C = [\mathrm{Br}]$, $D = [\mathrm{H}]$, $P = [\mathrm{HBr}]$ for doing your algebra.