

Dynamics of the Brusselator

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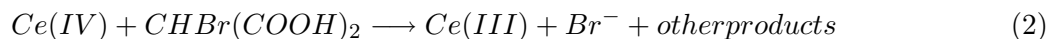
March 16, 2003

1 Introduction

The reaction mechanism to be studied, commonly called the Brusselator, is an example of an autocatalytic, oscillating chemical reaction. An autocatalytic reaction is one in which a species acts to increase the rate of its producing reaction. In many autocatalytic systems complex dynamics are seen, including multiple steady-states and periodic orbits.

The dynamics and chemistry of oscillating reactions has only been the subject of study for the last 50 years, starting with the work of Boris Belousov. Belousov was studying the Krebs's cycle when he stumbled upon an oscillating system. He witnessed a mixture of citric acid, bromate, and cerium catalyst in a sulfuric acid solution undergoing periodic color changes. These changes indicated the cyclic formation and depletion of differently oxidized cerium species [1]. The scientific community of the time believed that oscillations in a chemical system were disallowed by thermodynamic laws, so Belousov's work remained unpublished for years.

In 1961, ten years after Belousov's initial experiments, new work was initiated by A. M. Zhabotinskii. He quickly reproduced Belousov's results, and soon began working on a similar systems using malic or malonic acids as reductants. The system oscillations were measured by observing the optical density and the electrical potential of the solution as the oscillations occurred. Zhabotinskii demonstrated that Ce(III) and Ce(IV) were the cycling species, and he proposed a mechanism for how these cycles occurred. Equations (1) and (2) show the simplified mechanism.



Equation (1) is autocatalyzed by BrO_3^- , and strongly inhibited by Br^- ions. Therefore, as Ce(IV) is produced in equation (1) the rate of equation (2) increases. This results in a high concentrations of Br^- which inhibits and slows equation (1). First Ce(IV) concentrations drop, then Br^- concentrations drop, and the cycle begins again. (For a short review of chemical rate equations and their relationship to the individual species differential equations, see Section 2.)

This reaction system, now commonly referred to as the Belousov-Zhabotinskii (or B-Z) reaction has been thoroughly studied from both chemical and mathematical perspectives. It has also inspired a new areas of study, in both similar chemical systems and in the prediction of the behavior of complex reaction mechanisms. There are now a large number of both 'real' and 'toy' systems that provide insight into the complex behavior of autocatalytic oscillating systems. Among them are Lotka-Volterra, Oregonator, Edelstein, and Horn-Jackson example. We will be investigating the Brusselator, a hypothetical system. We will investigate the system's dynamics by observing behavior in the phase plane, proving the existence of stable cyclic orbits, and examining bifurcation properties.

2 Basics of Kinetic Equations

Chemical equations are commonly written in the following way:



indicating that species A and B react together to form species C and D. From the chemical equation we can easily write the rate equation. It is important to note that most chemical systems are assumed to follow mass action kinetics, meaning that the reaction rate is proportional to the concentration of the reactants.

$$-\dot{[A]} = -r_a = k[A][B] \quad (4)$$

In (4) $[A]$ represents the concentration of species A, r_a is the reaction rate, and k is the rate constant of the reaction. r_a is by convention negative since A is being consumed in the reaction. With only one reaction it is easy to see the differential equations governing the concentration of each species.

$$-\dot{[A]} = -\dot{[B]} = \dot{[C]} = \dot{[D]} = k[A][B] \quad (5)$$

By adding a second chemical equation we will demonstrate a slightly more complex system.



In equation (6) species A and E have stoichiometric coefficients greater than one. the differential equations for each species are now:

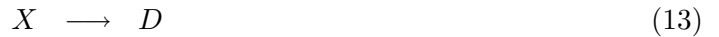
$$-\dot{[B]} = \dot{[C]} = \dot{[D]} = k[A][B] \quad (7)$$

$$\dot{[A]} = -k_3[A][B] - 2k_6[A]^2 \quad (8)$$

$$[\dot{E}] = 3k_6[A]^2 \quad (9)$$

Note that the rate gives the number of times that a reaction occurs in a volume at a given concentration, while the stoichiometric coefficient tells how many molecules of a species are consumed or produced in each reaction. For a more detailed lesson refer to [3].

The mechanism for the Brusselator is given by (10).



The two species of interest to us are X and Y, the autocatalytic species. The differential equations given in dimensionless form for these species are:

$$\dot{X} = 1 - (b + 1)X + aX^2Y \quad (14)$$

$$\dot{Y} = bX - aX^2Y \quad (15)$$

For this analysis all rate constants are assumed to equal 1, and the reactants A and B are assumed to be in large excess so that their concentrations do not change with time. The parameters a and b are thus also constant.

3 Dynamical Analysis

3.1 Equations

The dynamics of the Brusselator reaction can be described by a system of two ODE's. In dimensionless form, they are:

$$\dot{x} = 1 - (b + 1)x + ax^2y \quad (16)$$

$$\dot{y} = bx - ax^2y$$

where $x, y \in \mathbb{R}$, and $a, b \in \mathbb{R}$ are constants with $a, b > 0$. x and y represent the dimensionless concentrations of two of the reactants.

3.2 Equilibria

The equilibria of (16) are given by solving the system,

$$1 - (b + 1)x + ax^2y = 0 \quad (17)$$

$$bx - ax^2y = 0 \quad (18)$$

Adding (17) to (18) and simplifying gives $x = 1$. Plugging $x = 1$ into (18) gives $y = \frac{b}{a}$. Hence $(1, \frac{b}{a})$ is an equilibrium of the system, and in fact, the only equilibrium of the system.

3.3 Stability

Compute the Jacobian of the system:

$$Df(x, y) = \begin{pmatrix} -b - 1 + 2axy & ax^2 \\ b - 2axy & -ax^2 \end{pmatrix} \quad (19)$$

Evaluated at $(x, y) = (1, \frac{b}{a})$,

$$Df(1, \frac{b}{a}) = \begin{pmatrix} b - 1 & a \\ -b & -a \end{pmatrix} \quad (20)$$

To analyze the stability, we compute the trace and determinant of (20)

$$\tau = \text{Trace}\left(Df(1, \frac{b}{a})\right) = b - a - 1 \quad (21)$$

$$\Delta = \text{Det}\left(Df(1, \frac{b}{a})\right) = a \quad (22)$$

$\Delta > 0$, since $a > 0$, which implies that $(1, \frac{b}{a})$ is not a saddle point. If $b < a + 1$, then $\tau < 0$, and the equilibrium is an attractor. If $b > a + 1$, then $\tau > 0$, and it is a repeller. (See [1], pp. 136-137 for classification of fixed points using trace and determinant.) (see Figure 1)

3.4 Nullclines

Compute the \dot{x} -nullcline by setting $\dot{x} = 0$.

$$\begin{aligned} 1 - (b + 1)x + ax^2y &= 0 \\ \iff y &= \frac{(b + 1)x - 1}{ax^2} \end{aligned} \quad (23)$$

Compute the \dot{y} -nullcline by setting $\dot{y} = 0$.

$$\begin{aligned} bx - ax^2y &= 0 \\ x(b - axy) &= 0 \\ \implies x = 0 \quad \text{or} \quad y &= \frac{b}{ax} \end{aligned} \quad (24)$$

This nullcline consists of the y -axis and a hyperbola.

For $(a, b) = (1, 2.5)$, the nullclines are shown in Figure 2.

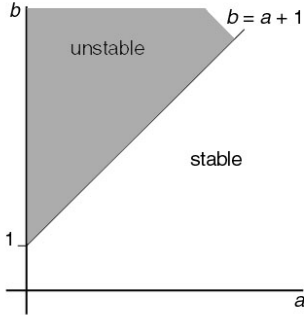


Figure 1: Stability analysis in parameter space

3.5 Bifurcation Analysis

First, fix a constant. As b varies, the equilibrium $(1, \frac{b}{a})$ undergoes a change in stability. Since there are no other equilibria in the system, it is reasonable to guess that a Hopf bifurcation occurs at $b_c = a + 1$. To prove this conjecture, we need to:

1. Show that the eigenvalues of (20) are pure imaginary and non-zero at $b_c = a + 1$, and
2. Show that the rate of change of the real part of the eigenvalues is non-zero at $b_c = a + 1$.

The eigenvalues of (20) will be pure imaginary and non-zero if and only if $\tau^2 - 4\Delta < 0$. From (21), $\tau = b - a - 1$. But, at $b_c = a + 1$, τ vanishes. From (22), $\Delta = a$. Thus, $\tau^2 - 4\Delta = -a < 0$, as required.

For an eigenvalue, λ , $\text{Re}(\lambda) = \frac{1}{2}\tau$. Since we fix a , we need $\partial\text{Re}(\lambda)/\partial b \neq 0$.

$$\frac{\partial\text{Re}(\lambda)}{\partial b} = \frac{1}{2} \frac{\partial}{\partial b} [b - a - 1] = \frac{1}{2} \neq 0, \quad (25)$$

as required. Hence, by I. and II., a Hopf bifurcation occurs at $b_c = a + 1$. (See [1], pp. 248-260 for Hopf bifurcation analysis).

3.6 Trapping Region

Next, to establish the existence of a periodic orbit, we need to construct a trapping region. Assume $b > a + 1$. Then $(1, \frac{b}{a})$ is a repeller. This implies that there exists a $\delta > 0$ such that all vectors on

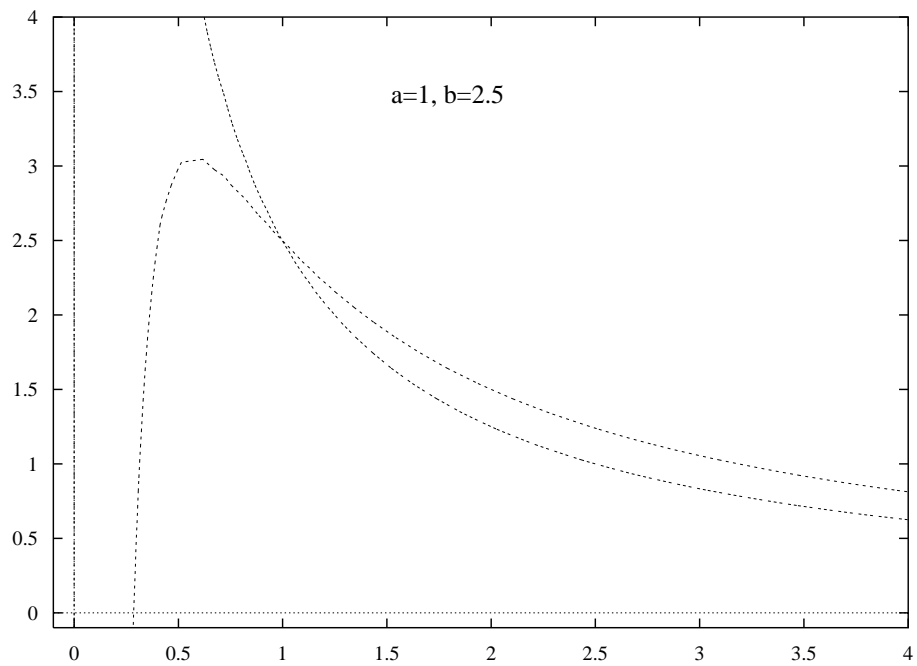


Figure 2: Nullclines of 16

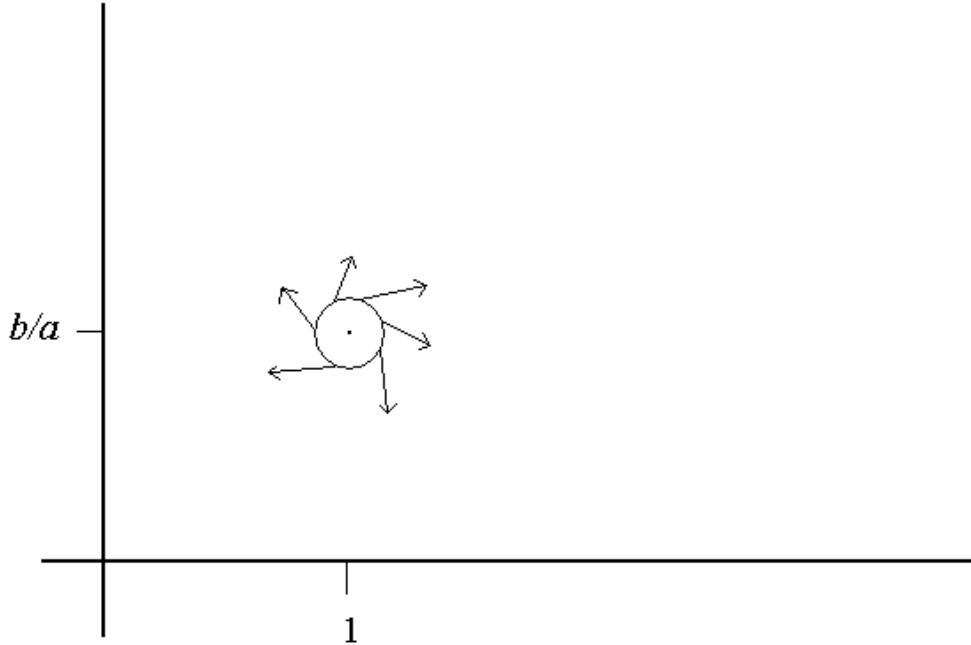


Figure 3: δ -neighborhood of the equilibrium

the boundary of the δ -ball centered at $(1, \frac{b}{a})$ must point to the exterior. (See Figure 3).

Now, consider the nullclines and the regions bounded by them in the first quadrant (Figure 4). We can use the x -axis as the lower boundary. The left boundary will need to intercept the x -axis at the point where the \dot{x} -nullcline intersects it so as to guarantee the flow in the correct direction. The x -intercept of the \dot{x} -nullcline is:

$$\begin{aligned} 1 - (b + 1)x + 0 &= 0 \\ \implies x &= \frac{1}{b + 1} \end{aligned} \tag{26}$$

Now, $b > 0$, so $b + 1 > 1$, and $0 < \frac{1}{b+1} < 1$, so we can use the line $x = \frac{1}{b+1}$ as the left boundary. Next, we want the upper boundary to meet the left boundary at its intersection point with the \dot{y} -nullcline. To find this point, we plug $x = \frac{1}{b+1}$ into (24):

$$y = \frac{b(b + 1)}{a} \tag{27}$$

$b > a + 1$ implies $y > 1$ in (27), so we can use the line $y = \frac{b(b+1)}{a}$ as the upper boundary. Now, if $k > 1$, the line $x = k$ can serve as the right boundary, however, it is only guaranteed to work between the x -axis and the \dot{x} -nullcline. (See Figure 5).

We need to construct a segment (the dotted line in Figure 5) which has the property that any vector on it will point towards the interior of the trapping region. Let $\mathbf{n} = (c_1, c_2)$ be a vector

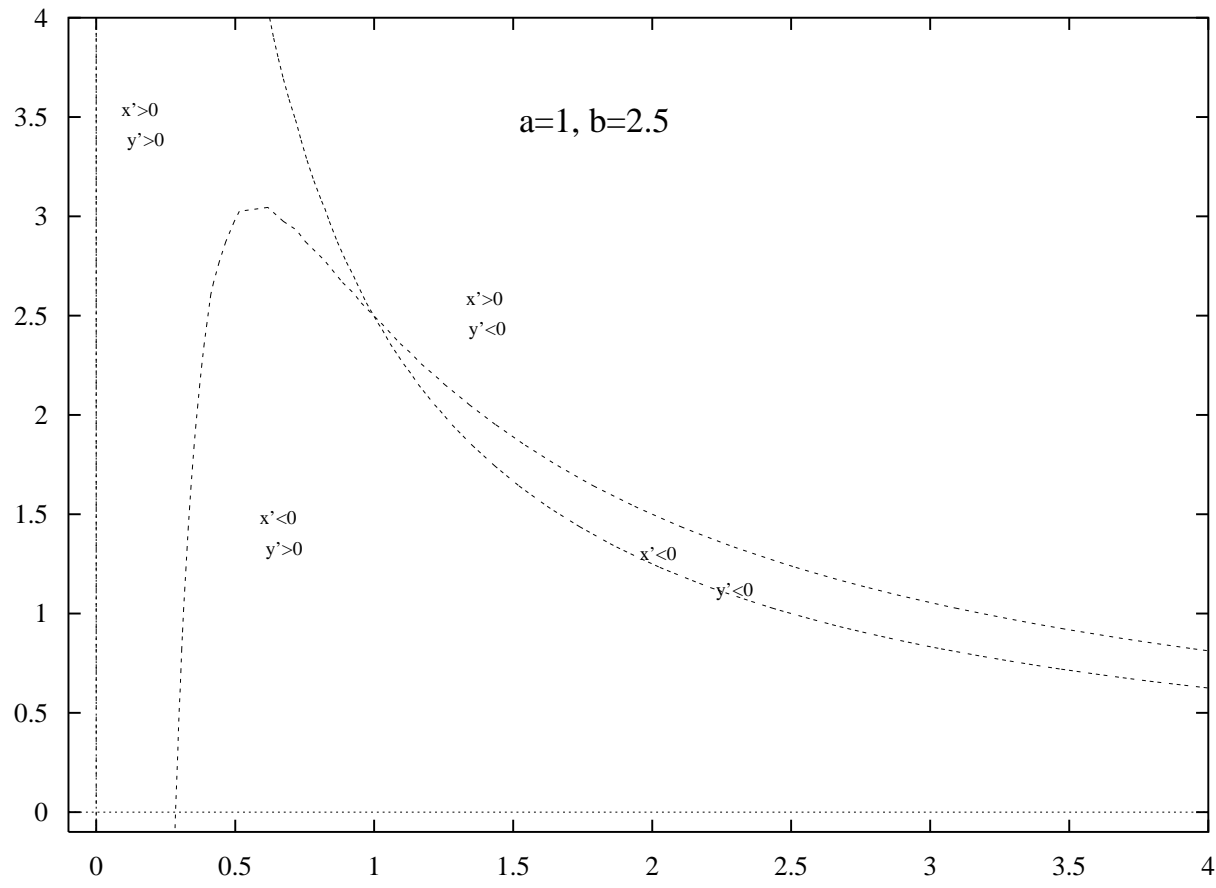


Figure 4: Flow regions

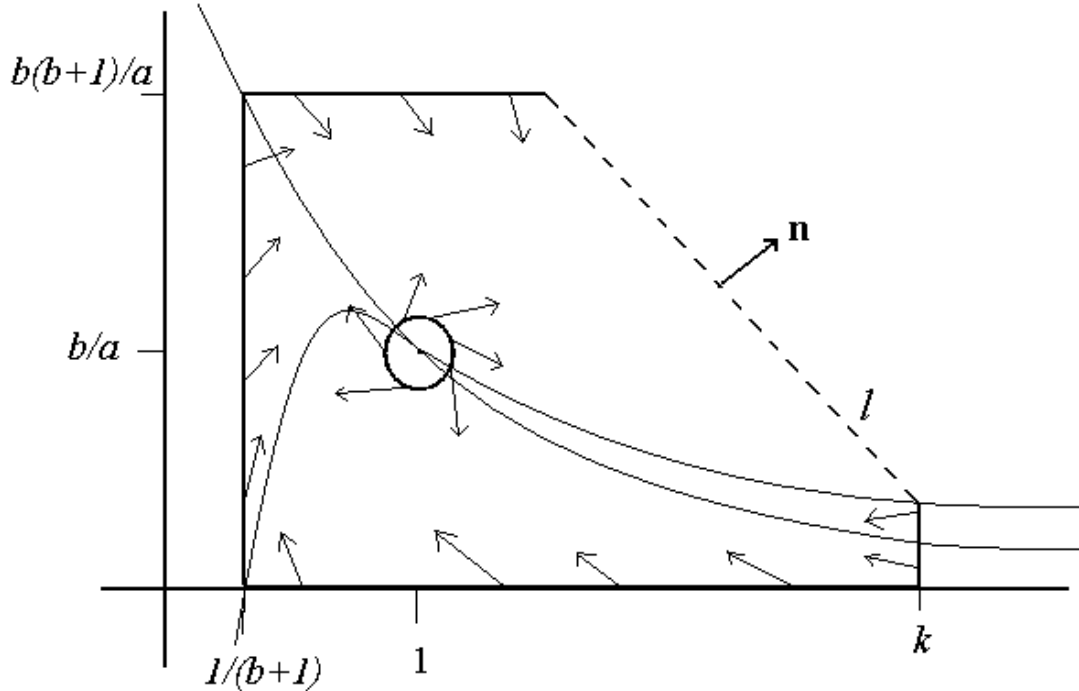


Figure 5: Trapping region

normal to the segment l . Then, we require

$$(c_1, c_2) \bullet (\dot{x}, \dot{y}) < 0 \quad (28)$$

Choosing $c_1 = c_2 = 1$, we write out (28), using (16):

$$1 - (b + 1)x + ax^2y + bx - ax^2y < 0 \quad (29)$$

After simplifying, we get

$$x > 1 \quad (30)$$

That is, as long as $x > 1$, the line with normal $(1, 1)$ will have the desired property. So, the upper-right boundary will be a line l of slope -1 , intersecting $x = k$ on the \dot{x} -nullcline (See Figure 6). We just have to choose k large enough so that the line l will intersect the upper boundary at a point with x -value greater than 1. But this is accomplished easily by requiring l to intersect $y = \frac{b(b+1)}{a}$ at $x = 2$, for example. Then at some point (with larger x -value), l will cross the x -axis. Therefore, there must be a point, $x = k$, at which it intersects the \dot{x} -nullcline (since the latter is positive for all $x > \frac{1}{b+1}$).

Having constructed a trapping region in which there are no equilibria, we can appeal to the Poincaré-Bendixson theorem to establish the existence of a periodic solution somewhere within the region. Also, since the periodic solution appears when the equilibrium destabilizes, this Hopf bifurcation is supercritical.

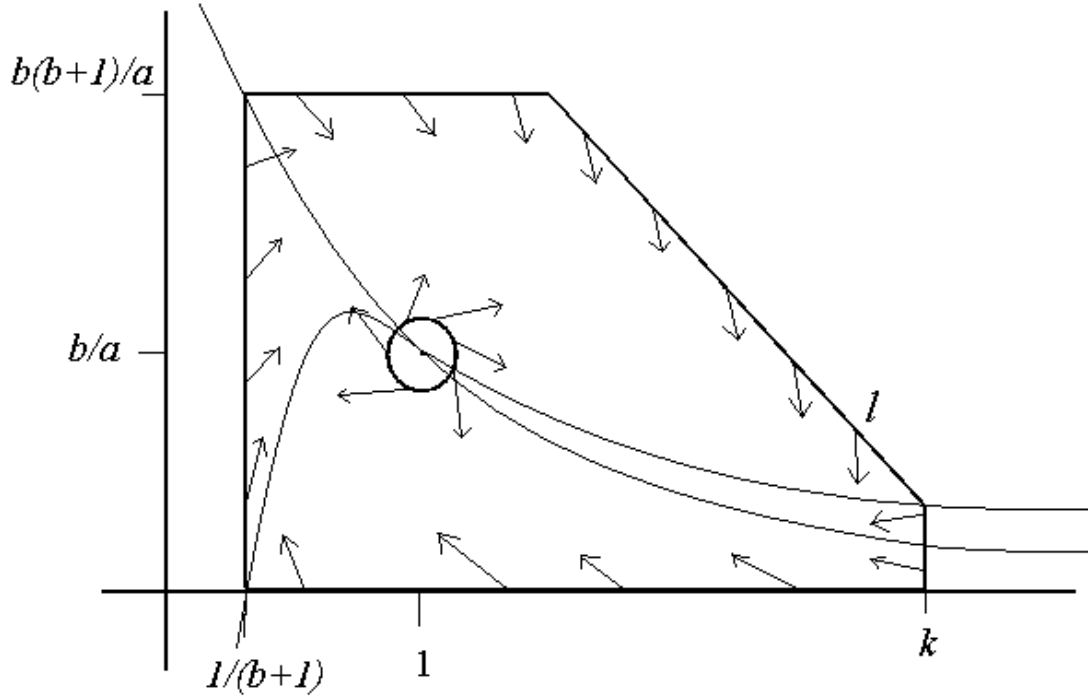


Figure 6: Trapping Region

3.7 Global Dynamics

We used XPP to investigate the behavior of solutions for various values of the parameters. Fixing $a = 1$, we vary b from 0.5 to 3.0, in increments of 0.5. For small b , the fixed point is stable, and attracts all orbits in the visible phase plane. As we increase b , the orbits make more turns around the equilibrium before finally converging. When $b = b_c = 2$, the equilibrium becomes neutral, and nearby trajectories do not seem to be attracted. It appears as though $(1, 2)$ is a non-linear center, although it could just be that the dynamics are stable or unstable on a much larger time scale. However, when b increases above 2, a stable limit-cycle appears, and the equilibrium is now a repeller. These dynamics continue for large b . (See figures...)

3.8 Period near $b_c = a + 1$

The approximate period of a periodic solution when b is near b_c is given by $2\pi/\omega$, where ω is the approximate frequency. We can find ω by calculating $|\text{Im}(\lambda)|$, where λ is an eigenvalue at $b = b_c$.

$$\lambda = \frac{1}{2}(\tau \pm \sqrt{\tau^2 - 4\Delta}) \quad (31)$$

At $b = b_c$, τ vanishes, so

$$\lambda_c = \pm i\sqrt{\Delta} \quad (32)$$

From (22) then,

$$\text{Im}(\lambda_c) = \sqrt{a} \quad (33)$$

and the approximate period is $2\pi/\sqrt{a}$.

References

- [1] Strogatz, Steven H., *Nonlinear Dynamics and Chaos*, Westview Press, 1994.
- [2] Field, Richard J., Burger, Maria, *Oscillations and Traveling Waves in Chemical Systems*, John Wiley and Sons, 1985.
- [3] Fogler, H. Scott, *Elements of Chemical Reaction Engineering*, Prentice Hall, 1999.

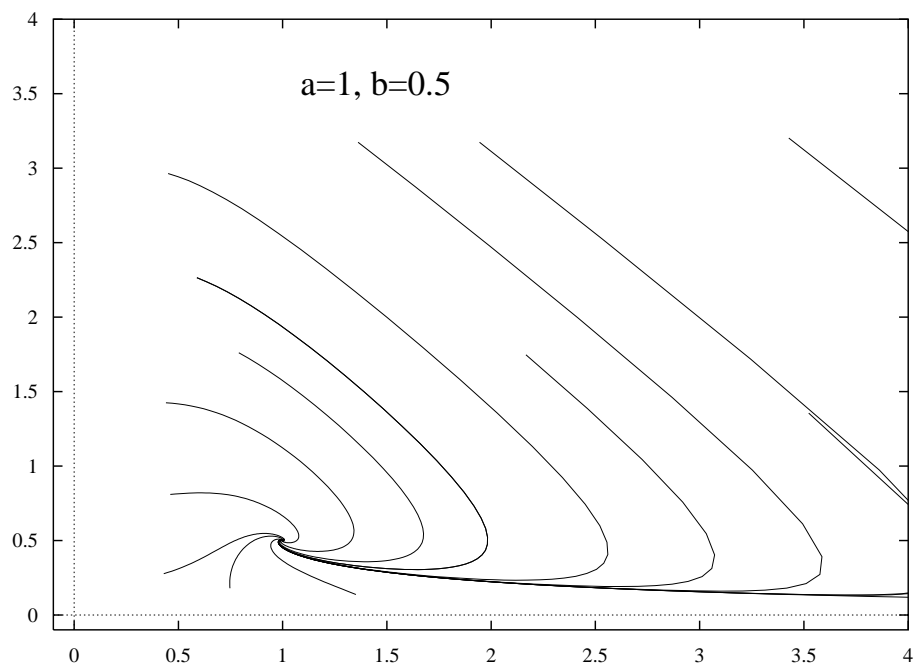


Figure 7:

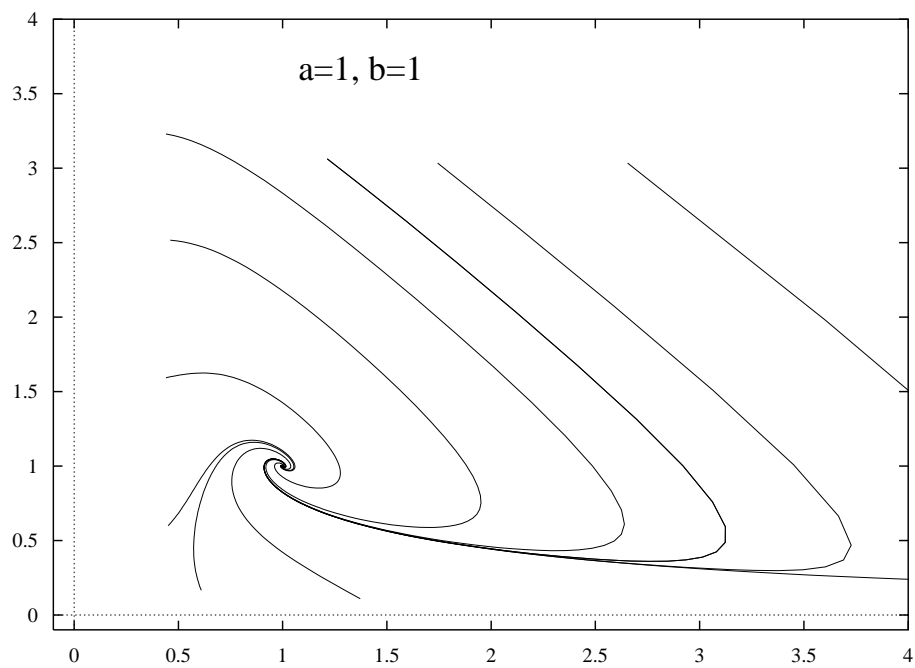


Figure 8:

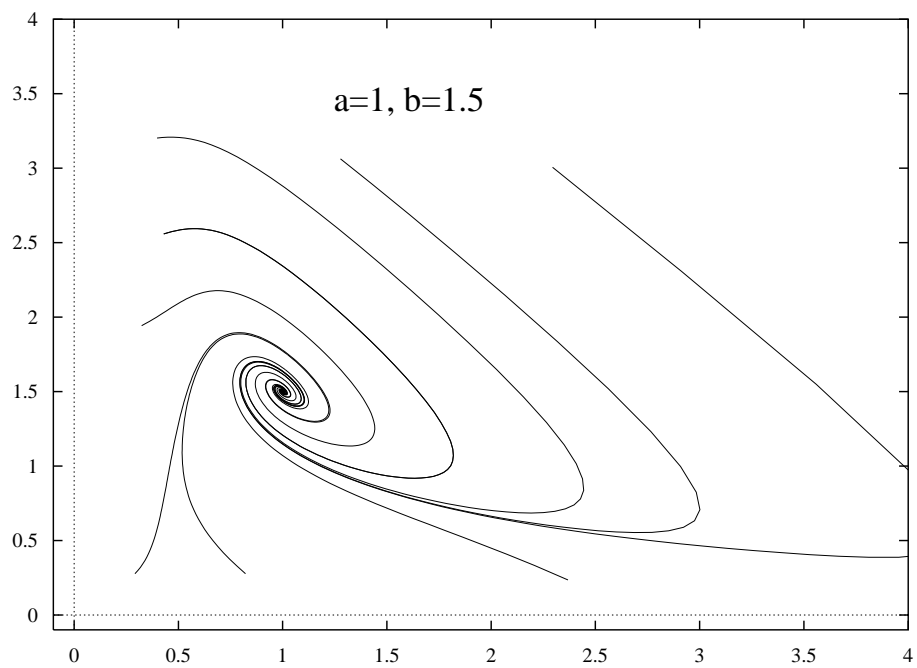


Figure 9:

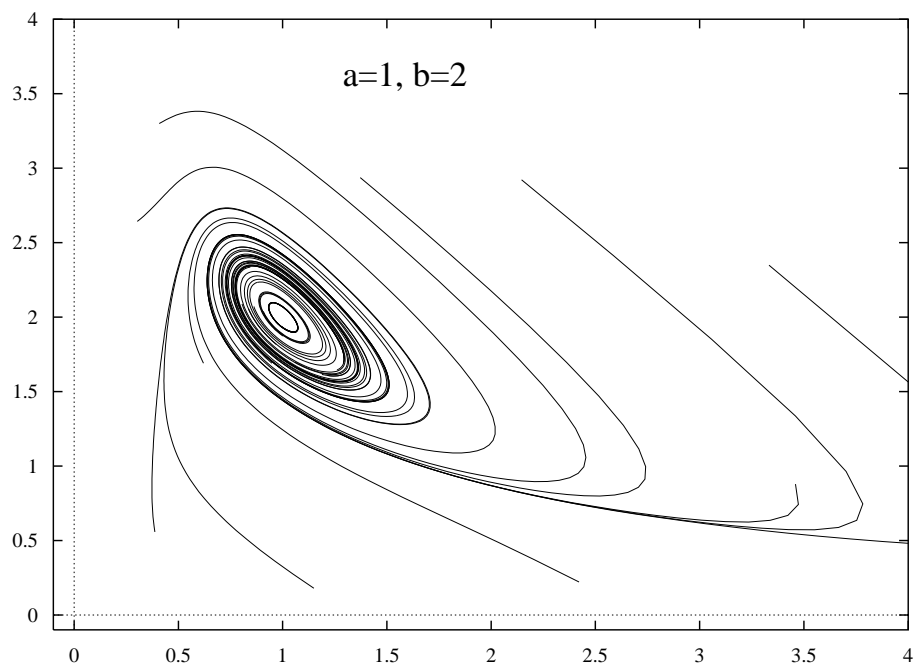


Figure 10:

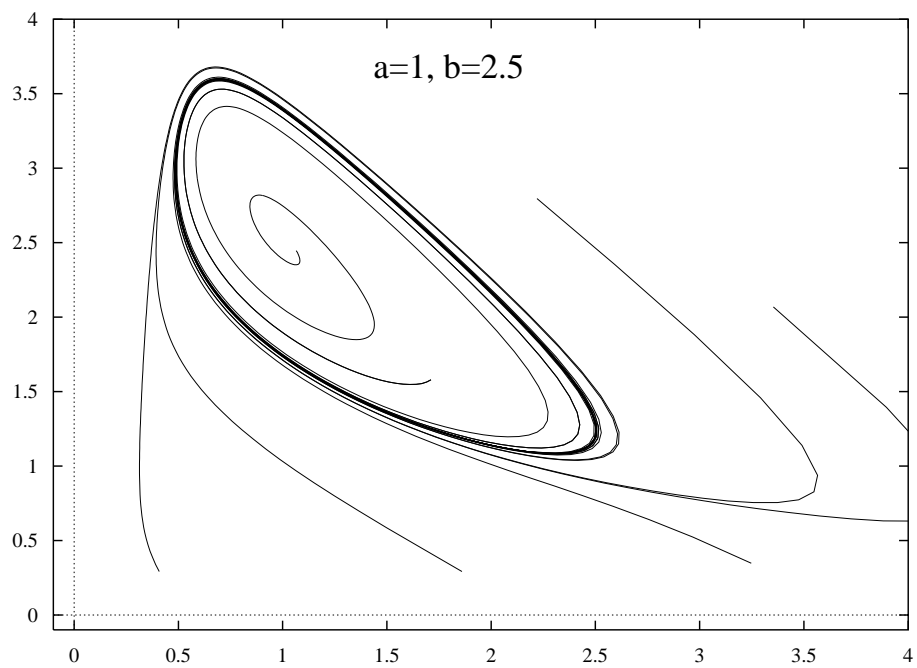


Figure 11:

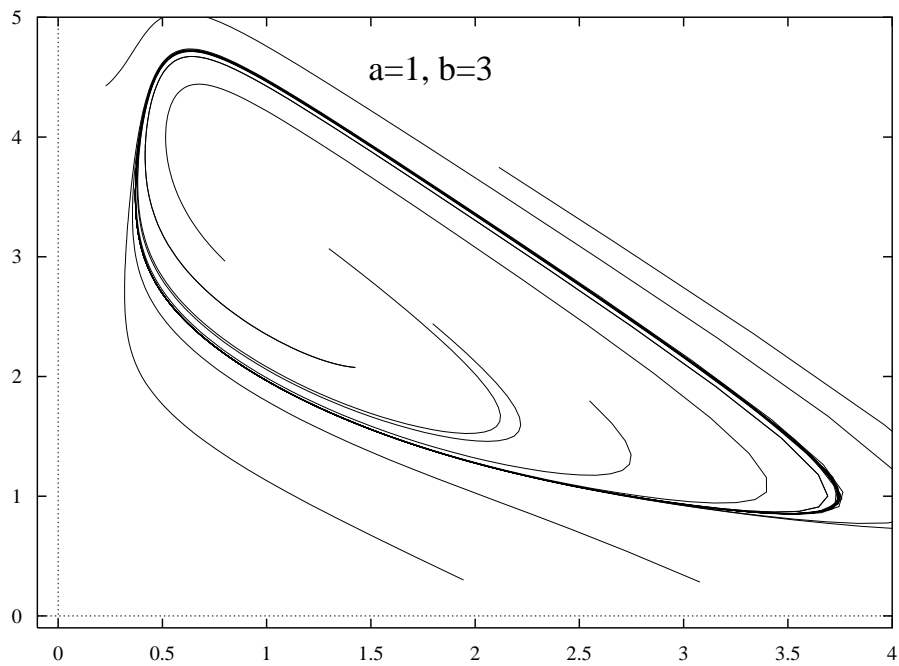


Figure 12: