Thermodynamics of Far-from-Equilibrium Systems: A Shift in Perception of Nature

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1 Introduction

In this report, I discuss two different topics of thermodynamics and explain how they have shaped the author's conception of science and nature. Nature used to be perceived as a predictable entity, which was governed by numerous sets of laws and equations. There was one point when scientists believed that with the knowledge of enough data, the future of the universe could be predicted considering that the universe can be reduced to a set of physical laws [3]. However, advances in the field of thermodynamics, especially the topic of dissipative structures, have shifted the scientific perception of nature. Through the lens of thermodynamics, nature appears to be a dynamical entity that "decides" its own path, and science turned out to be merely an attempt by humans to depict the way the universe works.

This paper is divided into three main parts. The first part will review the four basic laws of thermodynamics to provide a background for the following discussion in the next two parts. The second part will discuss the importance of the second law of thermodynamics and its implications for the limitations of science to describe nature. And finally, the third part will explore the non-linearity of nature through studying the model of weather simplified by Edward Lorenz [4], and the mathematical model of the Brusselator, a chemical reaction scheme created by Prigogine and several scientists at the Brussels School of Thermodynamics to study oscillations of non-linear chemical systems [2].

2 Thermodynamics review

Thermodynamics is studied based on four axioms.

2.1 The zeroth law

Although this law is numbered zero, it was in fact formulated after the other three laws since it is the implied assumption of the other three laws. The law can be expressed in the following statement:

If system A is in thermal equilibrium with system B, and system B is in thermal equilibrium with system C, then system A is in thermal equilibrium with system C.

2.2 The first law

The change in energy of a system is equal to the heat supplied to the system and work done by the system. The change in energy of adiabatic closed systems is zero.

The law can also be expressed by the following equation:

$$\Delta U = W - Q, \tag{2.2.1}$$

in which ΔU is the change in internal energy of the system, W is the work done (or undone) by the system, and Q is the change in heat supplied to the system. Equation (2.2.1) is written with the assumption that the change of mechanical energy of the system is small compared with its internal energy changes.

2.3 The second law

The total entropy of any isolated thermodynamic system, which is an indicator of how random a system is, tends to increase over time to approach a maximum value.

2.4 The third law

As temperature approaches absolute zero, the entropy of a system approaches a constant minimum.

3 Discussion of the second law

3.1 The need for the second law

Before the formulation of the second law of thermodynamics, the time reversal invariance of Newton mechanics affected the way scientists conceived nature: the physical events in the Newtonian realm can happen in both directions of time without violating the laws of mechanics. However, there were still some phenomena occurring in everyday life that cannot be explained by Newtonian laws at all. For example, why does the hot cup of coffee always cool as time progresses but never warm on its own? This hypothetical phenomenon can happen without violating the first law of thermodynamics: the heat from the surrounding environment can be used to warm the coffee, and in the heat engine case, the heat from the environment can be used to do work; therefore, the total energy of the system is conserved. The first law, however, fails to explain why we never observe that event in reality. There are many more phenomena observed in everyday life that can only happen in one direction. Why does the heat engine only take the heat from a hot environment to do work and release the unused heat to a colder environment? Why does it not take in the heat from the cold environment to do work and release unused heat to a hotter environment? Why does the amplitude of bouncing of a ball dropped on the ground decay as time progresses? Why do we never see broken pieces of a glass window reassemble themselves? These questions present a need for a law, a model that better describes the monotonic progress of nature. The second law of thermodynamics was formulated as a response to that need.

3.2 The second law and the Carnot's heat engine

Although the Second Law of Thermodynamics can be expressed in many different forms, perhaps the most well known form of the law is the Clausius statement. As time progresses, the entropy of an isolated system increases. Or, in mathematical form:

$$\frac{dS}{dt} \geq 0. \tag{3.2.1}$$

In equation (3.2.1), S is a the entropy of the system, which has the differential $dS = dQ/T$ for reversible processes. The quantity dQ is the heat change and T is the absolute temperature of the system. The differential dS is only equal to zero when the system undergoes an adiabatic reversible process. In irreversible processes, however, the relationship between S and the state values of the system is described by the inequality (3.2.2):

$$dS > \frac{dQ}{T}. \tag{3.2.2}$$

To illustrate this idea, let us consider a hypothetical reversible heat engine which was first introduced by Carnot [1]. This engine is perfectly designed so that the work it produces equals the difference of heat values between its cold state and its hot state: $W = Q_h - Q_c$

We then can derive an equation to calculate the efficiency of the Carnot heat machine:

$$\eta = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}. \tag{3.2.3}$$

For a reversible heat machine, $dS = 0$. This leads to: $Q_c/Q_h = T_c/T_h$. Equation (3.2.3) then becomes:

$$\eta = \frac{W}{Q_h} = 1 - \frac{T_c}{T_h}. \tag{3.2.4}$$

Equation (3.2.4) shows that the Carnot engine can only achieve full efficiency when the temperature of the cold reservoir is absolute zero. This, of course, can never be achieved in practice, and full efficiency cannot be reached. Because the Carnot engine is an ideal one, its efficiency places an upper limit on all other heat machines. Before Carnot's time, people believed that achieving full efficiency was just a matter of design: better designs with less friction would increase the efficiency of systems. However, the second law of thermodynamics, and its application in the Carnot engine case have shown that even a perfect machine cannot run at full efficiency. The author came to a realization that humans, once thinking they could finally harness the forces of natures, still have to play by its rule.

4 Nature as a dynamic entity

Traditional thermodynamics focuses on the study of closed, isolated systems which, if given enough time, always approach stable equilibrium states. Nature, however, is an assemblage of many different open systems which, when driven by the continuous flow of matter and energy, are far from equilibrium and often develop into a multitude of states. Since the study of science is not complete until it forms a connection with our everyday experience, it is necessary for us to depart from traditional thermodynamics to step into the study of far-from-equilibrium thermodynamics in order to have a more complete understanding of nature. In this section, we will discuss the development of thermodynamics from the linear, equilibrium realm to the non-linear realm by studying chemical kinetics. This discussion consists of three sections. The first section serves as a review of traditional thermodynamics through studying a one-step reaction. In the second section, we have our first taste of modern thermodynamics by studying the oscillating behavior of the famous Brusselator system. Finally, we will see a more complex thermodynamical system through analyzing chaos modeled by the Lorenz's equations.

4.1 A review of traditional thermodynamics

Let us consider the following chemical reaction:

$$X + 2Y \rightleftharpoons 2Z. \tag{4.1.1}$$

Let $[X], [Y], [Z]$ be the concentrations of substances X, Y, Z respectively. By using the law of mass action for reaction (4.1.1), we can define the following system of differential equations

$$\begin{aligned} \frac{d[X]}{dt} &= -k_f[X][Y]^2 + k_r[Z]^2, X[0] = X_0, \\ \frac{d[Y]}{dt} &= -2(k_f[X][Y]^2 + k_r[Z]^2), Y[0] = Y_0, \\ \frac{d[X]}{dt} &= 2(k_f[X][Y]^2 - k_r[Z]^2), Z[0] = Z_0. \end{aligned} \tag{4.1.2}$$

With $k_f = 0.5, k_r = 0.05, X_0 = 2.0, Y_0 = 3.0, Z_0 = 0$, we can then use the software tool `Mathematica` to generate numerical solutions for the above system of equations. Plots of $[X], [Y], [Z]$ as functions of time are shown in Figure 1:

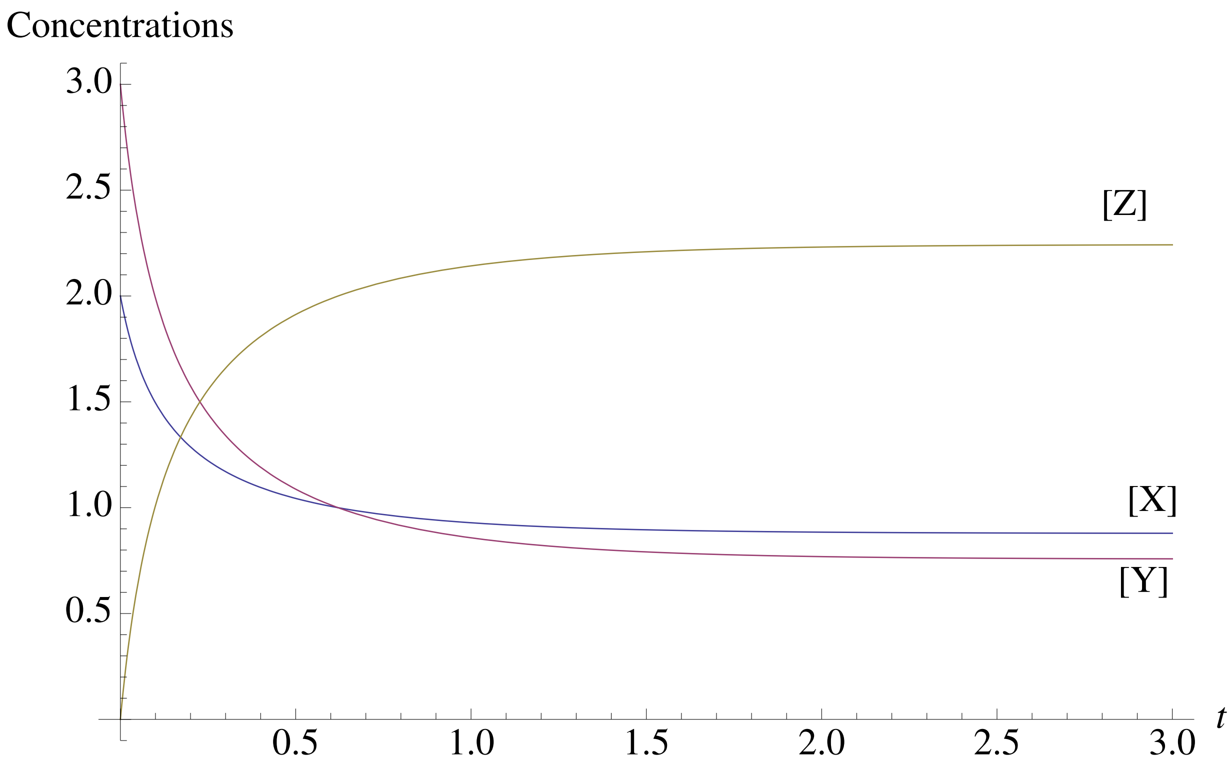

Figure 1: Concentrations of X, Y, Z as time progresses.

As Figure 1 shows, as the time progresses, the concentrations of the chemicals approach constant values. The general development of the reaction can be better seen with the parametric plot of the concentrations:

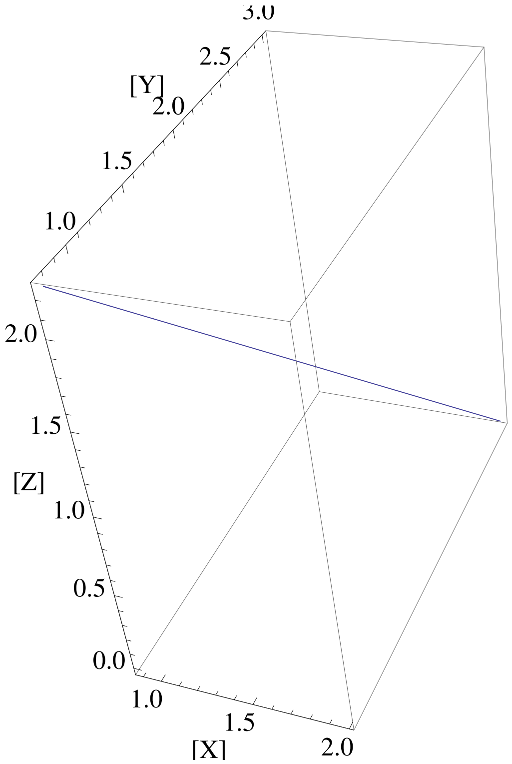

Figure 2: Parametric plot of $[X]$, $[Y]$, $[Z]$.

The parametric plot featured in Figure 2 shows a monotonic process that is typical for systems approaching equilibrium states. Also, it was found out that small changes in the initial conditions do not affect the general trend of the reaction. Since all the reaction monotonically approaches equilibrium as time increases, it is easy to predict the outcomes of chemical processes in the realm of classical thermodynamics. However, it was discovered that in reality, instead of approaching constant values, concentrations of chemicals can sometimes oscillate, which create many observed patterns in nature. This oscillation can be studied by analyzing the Brusselator, a simple model created by Prigogine and Lefever when they started to look into the behavior of non-linear chemical systems that are organized by thermodynamical forcings governed by the extremum principles.

4.2 The Brusellator and oscillating chemical reactions

The Brusselator is characterized by the following reaction scheme:

$$\begin{aligned} A \rightarrow &\quad X, \\ B + X \rightarrow &\quad Y + D, \\ 2X + Y \rightarrow &\quad 3X, \\ X \rightarrow &\quad E. \end{aligned} \tag{4.2.1}$$

If we assume that there is an infinite constant flow of A and B into the system, and D and E are removed, we will have the following system of equations of concentrations of X and Y:

$$\begin{aligned} \frac{d[X]}{dt} &= k_1[A] - k_2[B][X] + k_3[X]^2[Y] - k_4[X] \equiv Z_1([X],[Y]), \\ \frac{d[Y]}{dt} &= k_2[B][X] - k_3[X]^2[Y] \equiv Z_2([X],[Y]). \end{aligned} \tag{4.2.2}$$

By setting Z_1 and Z_2 equal to 0, it is easy to calculate the stationary solutions to system 4.2.3:

$$[X]_s = \frac{k_1}{k_4}[A], \qquad [Y]_s = \frac{k_4 k_2}{k_3 k_1}\frac{[B]}{[A]}, \tag{4.2.3}$$

in which k_1, k_2, k_3, k_4 are the respective reaction constants of the elementary reactions in the system. In order to know at what values of $[A]$ and $[B]$ and reaction rate constants the system will shift to the oscillating state, we need to analyze the eigenvalues of the Jacobian matrix of system 4.2.2:

$$\begin{bmatrix} k_2[B] - k_4 & k_3[X]_s^2 \\ -k_2[B] & -k_3[X]_s^2 \end{bmatrix}. \tag{4.2.4}$$

The eigenvalues of matrix 4.2.4 are calculated by equation 4.2.5:

$$\lambda^2 - (k_2[B] - k_4 - k_3[X]_s^2)\lambda + [X]_s^2(-k_2k_3[B] + k_4k_3 + k_3k_2[B]) = 0. \tag{4.2.5}$$

The system is only unstable when at least one of the eigenvalues has a positive real part. For this to happen, inequality (4.2.6) must be satisfied:

$$[B] > \frac{k_4}{k_2} + \frac{k_3k_1^2}{k_2k_4^2}[A]^2. \tag{4.2.6}$$

With $k_1 = k_2 = k_3 = k_4 = 1.0, [A] = 1.0, [B] = 3.0$, we satisfy inequality (4.2.6). We use these values to plot the graphs of the concentrations as functions of time in Figure 3:

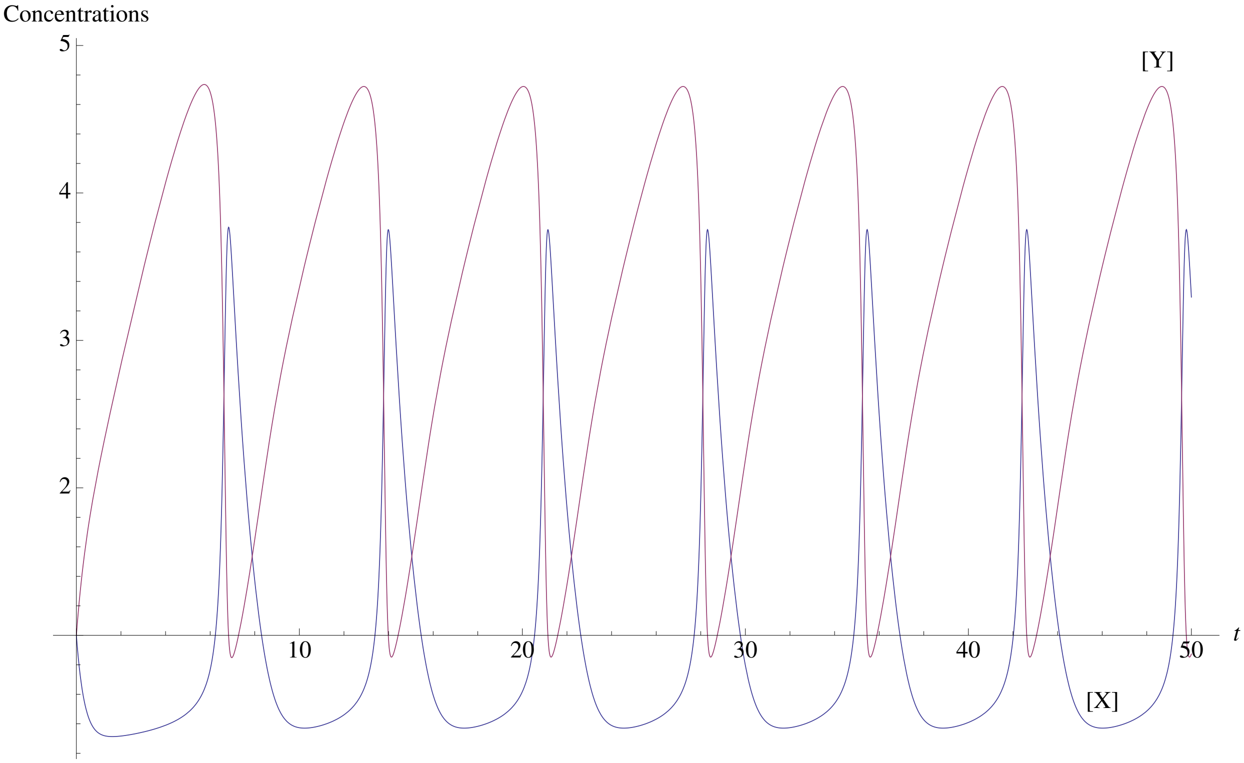

Figure 3: Oscillations of $[X]$ and $[Y]$ as time progresses.

To see the general progress of the system, let us examine its limit cycle projected on the phase plane in Figure 4:

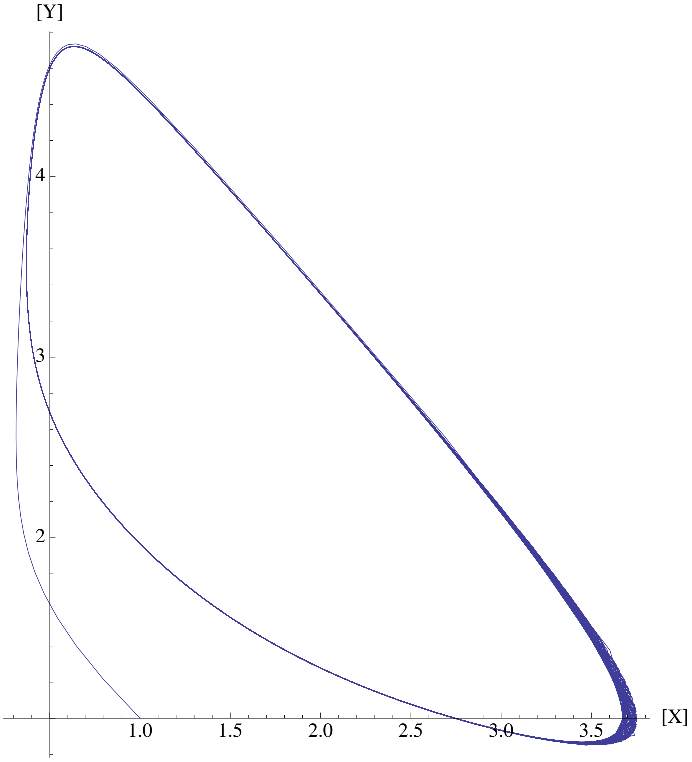

Figure 4: Parametric plot of $[X]$ and $[Y]$.

Figure 4 shows that the Brusselator begins with non-periodic changes of concentrations and spirals into a periodic limit cycle as time progresses. Unlike system (4.1.1), this reaction scheme is sustained by a constant supply of external matters, in this case A and B, which destabilizes the concentrations of X and Y and make them oscillate as time progresses.

Also, while small change in initial conditions do not affect traditional thermodynamics systems, a small change in the supply of A and B can also shift the Brusselator into another state. For example, the system does not spiral into a limit cycle if $[B] = 1.9$, as illustrated by Figure 5:

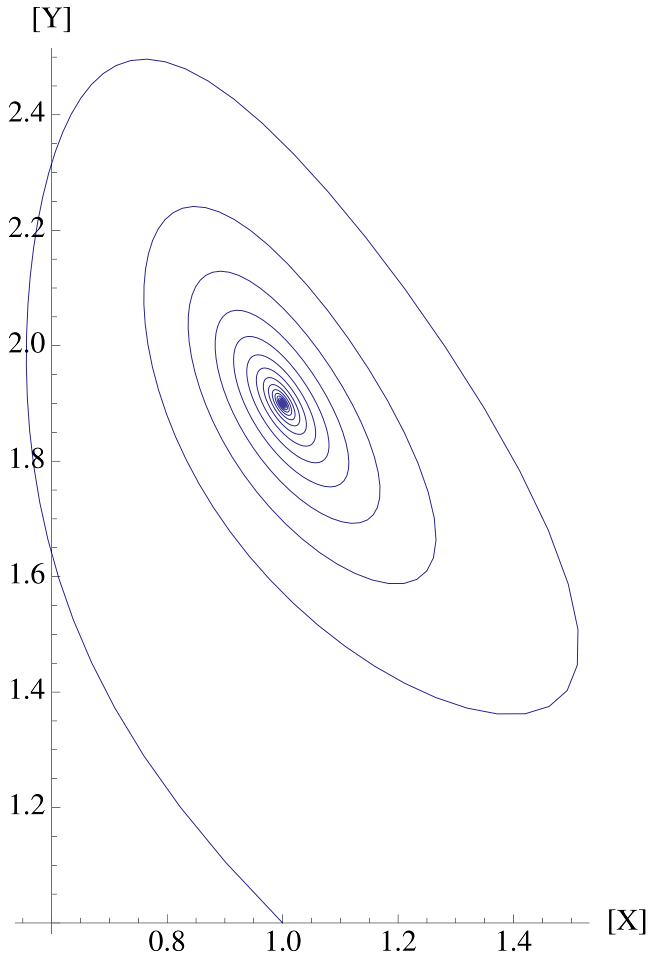

Figure 5: Parametric plot of [X] and [Y].

Figure 5 shows that that instead of spiraling into a limit cycle, the system spirals into a single point as time progresses. As a result, the concentrations of X and Y oscillate with decreasing magnitude and become stable as time approaches infinity. The graphs of the concentrations of X and Y are shown in Figure 6:

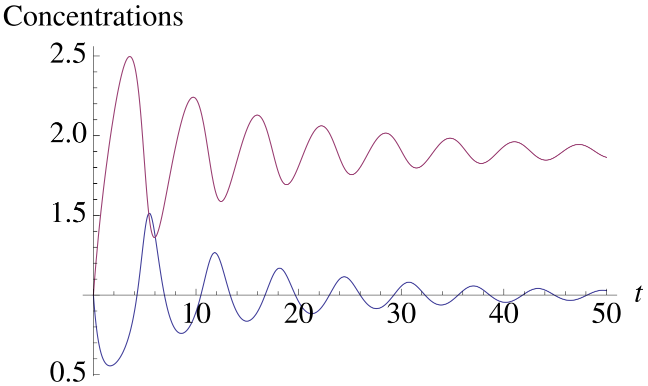

Figure 6: Oscillations of $[X]$ and $[Y]$ as time progresses.

Therefore, in far-from-equilibrium chemical systems like the Brusselator, small perturbations in the flow of matter into the systems can shift them to different states. The oscillations of these systems in nature create patterns that we can observe. Figure 7 features the pattern observed during the Belousov-Zhabotinsky reaction [5], a reaction which is also a non-linear oscillator.

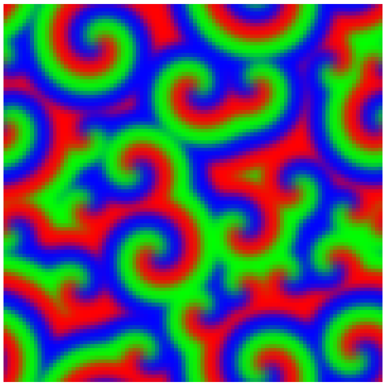

Figure 7: Belousov chemical reaction.

In the next section, we will take one more step to explore chaotic systems by looking into the Lorenz's system, which is a simplified model of weather.

4.3 A chaotic nature

In section 4.1, we learn that chemical reactions within the traditional thermodynamics realm monotonically progress into stable states, in which the concentrations of the participating chemicals remain constant. In section 4.2, we move into studying far-from-equilibrium systems through the Brusselator model. We learn that some systems in nature can oscillate in a periodic fashion while others can oscillate into a decaying mode depending on the inflow of matter into the systems. In this section, we will look at Lorenz's model and its implications for a chaotic nature.

During the 1960's, after the advent of computers, meteorologists believed that accurate long-range weather forecast would be achieved eventually if enough data about weather was collected. At that time, scientists paid more attention to the statistics of turbulence in weather, which, in contrast to the details of turbulence, are more organized. However, Edward Lorenz disproved this belief in 1963 with his paper on deterministic non-periodic flow. By studying the simple problem of convective motion of fluid, Lorenz was able to point out that the solutions to some non-linear hydrodynamical systems vary in a "haphazard manner" (Lorenz, 1963). and small perturbations in external forcings can result in a drastically different evolution of the system.

In his paper, Lorenz revisits the fluid convection problem studied by Rayleigh. In this problem, the motion of a layer of fluid, which has a depth of H and a temperature difference of ΔT between its upper and lower surface, is analyzed. After expanding and using different variables to transform the convective equations, Lorenz presented the following system of differential equations:

$$\begin{aligned} \frac{dX}{dt} &= -\sigma X + \sigma Y, \\ \frac{dY}{dt} &= -XZ + rX - Y, \\ \frac{dZ}{dt} &= XY - bZ. \end{aligned} \tag{4.3.1}$$

in which X is proportional to the intensity of the convective motion, while Y is proportional to the temperature difference between the ascending the descending currents, and Z is proportional to the distortion of vertical temperature profile from linearity. With $\sigma = 5.8, r = 28, b = 8/3$, we can graph the parametric curve of X, Y, Z as time changes:

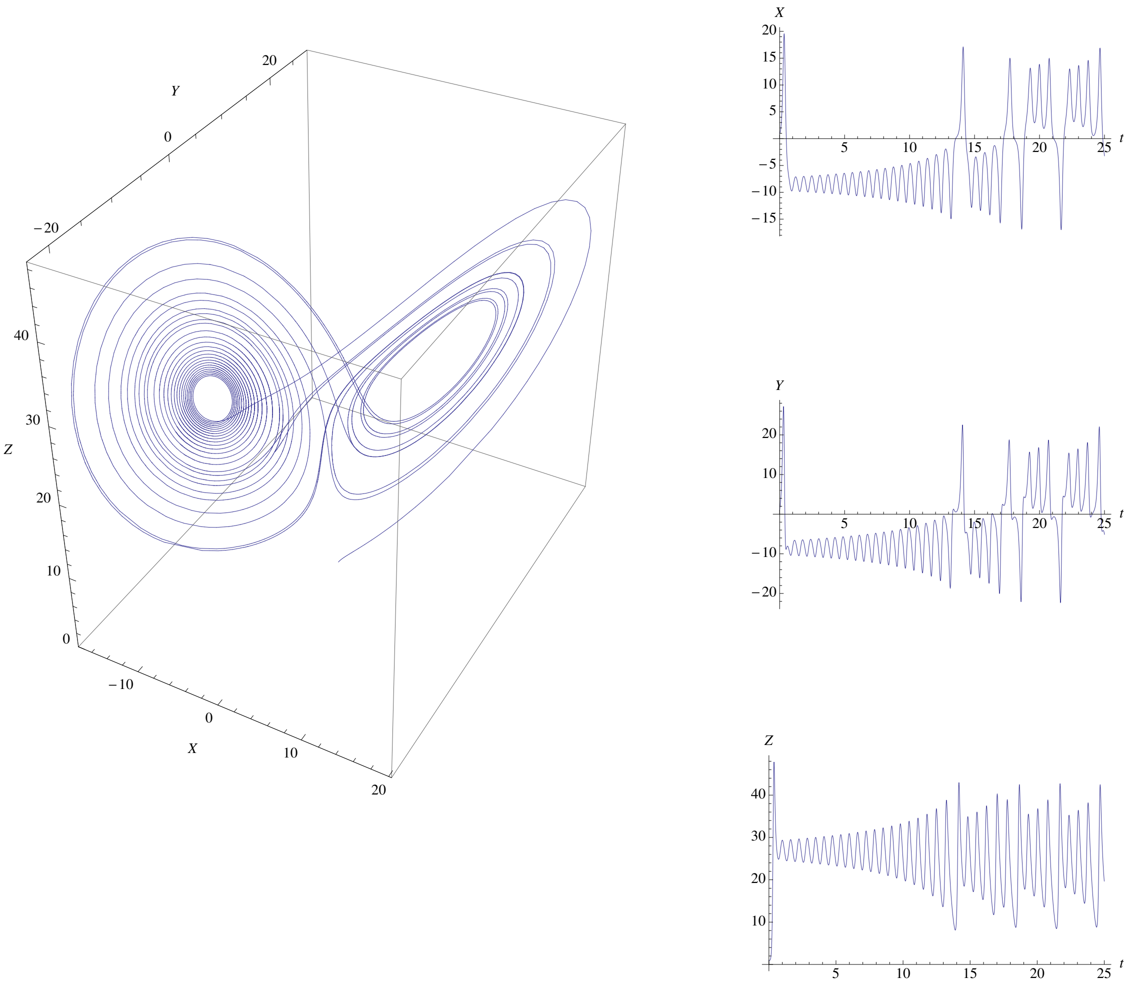

Figure 8: Chaotic evolution of the system.

As shown in Figure 8, this parametric curve of the system exhibits a non-periodic characteristic: it never catches its "tail". As time progresses, the curve neither spirals into a point or a limit cycle or spirals out in an organized manner. However, with small perturbations in external forcings, the system can go back to a decaying mode. For example, with $r = 5.6$, the parametric curve spirals into a point again, as shown in Figure 9:

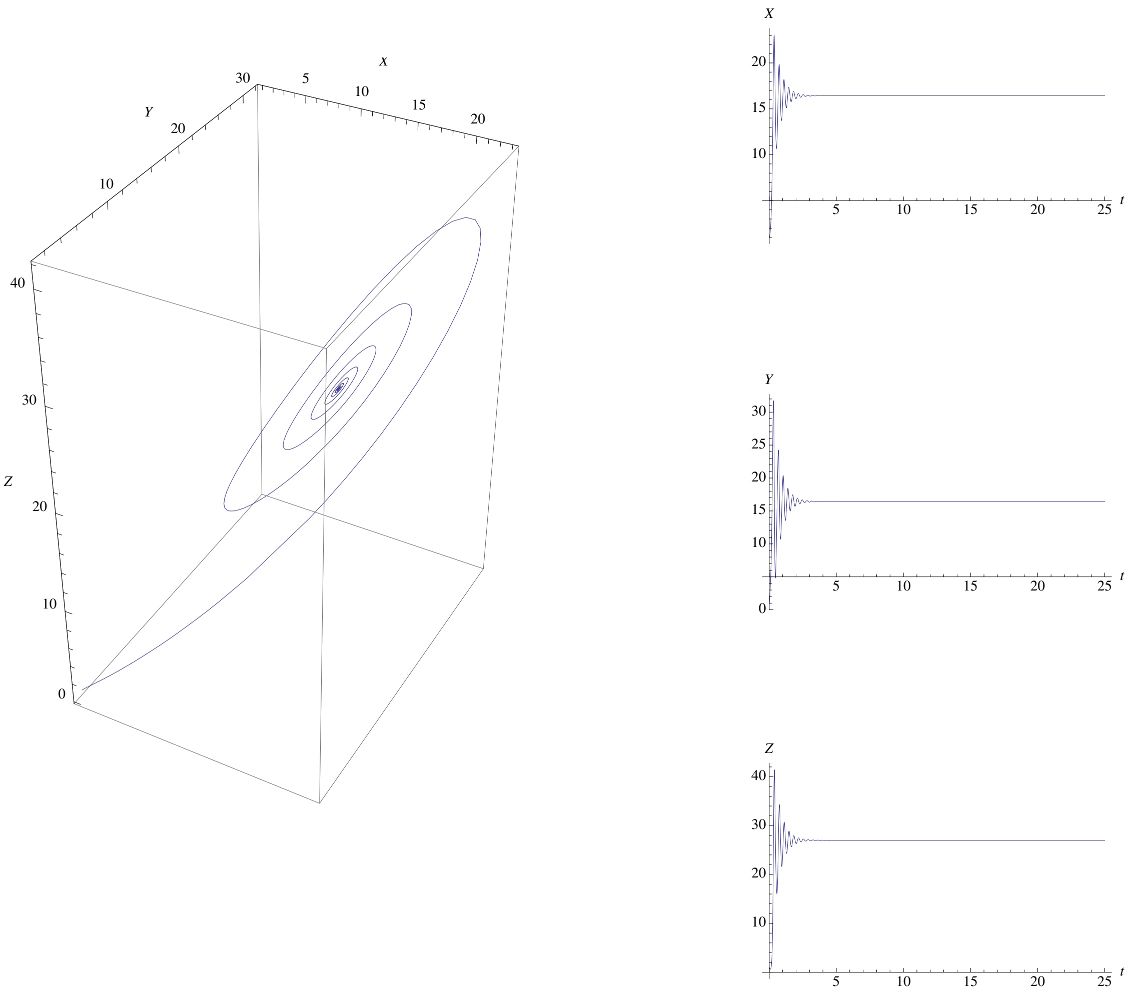

Figure 9: Decaying System.

Because weather is much more complicated than this hydrodynamical model, small variations in nature can turn a highly organized state of weather to complete chaos, in which predictions are impossible. Lorenz's model is often called the "butterfly effect," a name which refers to the idea that the flap of a butterfly's wings in one place can result in large-scale weather events in other places due to the non-linear nature of weather. Therefore, long-range weather forecast remains an elusive dream of mankind.

5 Conclusion

Science is the tool of humans to depict the way the universe works. The legalistic connotation of the word "law" in science, as in "Newton's Laws", "Ohm's Law", gives many people, including the author, the false impression that nature is dictated by equations and laws, and that our future is determined before the world came into being. The study of modern thermodynamics throughout this course, however, has proved that nature is independent our perception, and it is able to decide its own path. This realization moves people to the positive view that they can still be an agent of change through our interaction with nature. Despite its powerful capability to describe nature, science can never substitute our experience of nature.

References

[1] Carnot, S., 1824, *Reflexions sur la Puissance Motrice du Feu et sur les Machines propres a Developper cette Puissance*, Bachelier, Paris. (English translation, 2005, *Reflections on the Motive Power of Fire*, Dover, Mineola, New York). 1897 English translation.

[2] Kondepudi, D. and I. Prigogine, 1998, *Modern Thermodynamics: From Heat Engines to Dissipative Structures*, John Wiley and Sons, New York.

[3] Laplace, M. and S. Pierre, 1814, *A Philosophical Essay on Probabilities*, John Wiley and Sons, London.

[4] Lorenz, E. N., 1963, "Deterministic Nonperiodic Flow." *Journal of the Atmospheric Sciences* , 20(2): 130-141.

[5] "*Provotis - Examples.*" *Stanford Visualization Group.* Web. 11 Dec. 2010. http://vis.stanford.edu /provotis/ex

Appendix 1: Mathematica code for figures 1 and 2

```
kf = 0.5;
kr = 0.05;
e1 = X’[t] == -kf*X[t]*Y[t]^2 + kr*Z[t]^2;
e2 = Y’[t] == 2*(-kf*X[t]*Y[t]^2 + kr*Z[t]^2);
e3 = Z’[t] == -2*(-kf*X[t]*Y[t]^2 + kr*Z[t]^2);
SOL = NDSolve[{e1, e2, e3, X[0] == 2.0, Y[0] == 3.0, Z[0] == 0.0}, {X, Y, Z},
{t, 0, 3}]
Plot[Evaluate[{X[t], Y[t], Z[t]} /. SOL], {t, 0, 3}, PlotRange -> All, AxesLabel
→ {t, Concentrations}, BaseStyle → {FontSize → 14}] %figure 1
ParametricPlot3D[Evaluate[{X[t], Y[t], Z[t]} /. SOL], {t, 0, 3}, PlotRange
→ All, AxesLabel → {"[X]", "[Y]", "[Z]"}, BaseStyle → {FontSize → 14}] %figure
2
```

Appendix 2: Mathematica code for figures 3 and 4

```
k1 = 1.0;

k2 = 1.0;

k3 = 1.0;

k4 = 1.0; A = 1;

B = 3;

Soln2 = NDSolve[{X'[t] == k1*A - k2*B*X[t] + k3*(X[t])^2*Y[t] - k4*X[t], Y'[t]
== k2*B*X[t] - k3*(X[t])^2*Y[t], X[0] == 1.0, Y[0] == 1.0}, {X, Y}, {t, 0, 400}];

Plot[Evaluate[{X[t], Y[t]} /. Soln2], {t, 0, 50}, PlotRange -> All, AxesLabel
-> {t, Concentrations}, BaseStyle -> {FontSize -> 14}]

ParametricPlot[Evaluate[{X[t], Y[t]} /. Soln2], {t, 0, 400}, PlotRange ->
All, AxesLabel -> {"[X]", "[Y]"}, BaseStyle -> {FontSize -> 14}] %figure 4
```

Appendix 3: Mathematica code for figures 5 and 6

```
k1 = 1.0;

k2 = 1.0;

k3 = 1.0;

k4 = 1.0;

A = 1.1;

B = 2;

Soln2 = NDSolve[{X’[t] == k1*A - k2*B*X[t] + k3*(X[t])^2*Y[t] - k4*X[t], Y’[t] == k2*B*X[t] - k3*(X[t])^2*Y[t], X[0] == 1.0, Y[0] == 1.0}, {X, Y}, {t, 0, 400}];

Plot[Evaluate[{X[t], Y[t]} /. Soln2], {t, 0, 50}, PlotRange -> All, AxesLabel -> {t, Concentrations}, BaseStyle -> {FontSize -> 14}]

ParametricPlot[Evaluate[{X[t], Y[t]} /. Soln2], {t, 0, 400}, PlotRange -> All, AxesLabel -> {"[X]", "[Y]"}, BaseStyle -> {FontSize -> 14}] %figure 5
```

Appendix 4: Mathematica code for figures 8 and 9

```
eqs = {x’[t] == 10 (y[t] - x[t]), y’[t] == 28 x[t] - y[t] - x[t] z[t], z’[t] == -8/3 z[t] + x[t] y[t], x[0] == y[0] == z[0] == 1}

solv = NDSolve[eqs, {x, y, z}, {t, 0, 25}]

ParametricPlot3D[Evaluate[{x[t], y[t], z[t]} /.  solv], {t, 0, 25}, PlotRange -> All] %figure 8

eqs = {x’[t] == 10 (y[t] - x[t]), y’[t] == 28 x[t] - y[t] - x[t] z[t], z’[t] == -10 z[t] + x[t] y[t], x[0] == y[0] == z[0] == 1}

ParametricPlot3D[Evaluate[{x[t], y[t], z[t]} /.  solv], {t, 0, 25}, PlotRange -> All] %figure 9
```