Entropy Production of the Earth System

A thesis submitted in partial fulfillment of the requirements
for the degree of Master of Science in Mathematics

by

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December 2015
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Dedication

For my family
Acknowledgments

I was very lucky to have found Professor David Klein. To have seen his dedication to mathematics, education, and welfare of society is inspirational.

Of course, I’m very thankful for the support received from my family.
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Abstract

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Thermodynamic aspects of the long-term mean properties of the global climate system and turbulent fluid systems are reviewed. The necessary background material of thermodynamics and the climate system are introduced. General expressions are found for the rate of entropy production for a fluid system undergoing turbulence. These expressions show that the Earth’s climate system correspond to state of maximum entropy production due to the dissipation of heat from turbulent fluids. This was applied to the long-term mean of the global climate by Garth Paltridge. The Earth’s climate is driven and maintained by radiation exchanges with space. The absorption of solar radiation is the main source of entropy production; however, this appears to be irrelevant to the maximized properties associated with turbulence. The results tend to support the hypothesis of the maximum entropy production that include a large range of nonlinear fluid systems.
Chapter 1

Introduction

Earth’s climate has changed over the industrial period as seen by increasing global surface temperatures and rising sea levels. The main cause of this is due to greenhouse gas emissions. The consequences of climate change are expected to be huge, which can include creating an inhospitable environment, increase in the number of extreme weather events such as droughts, fires, and floods, and changes in the water resources and ecosystems. Protecting Earth’s habitable environment requires understanding Earth’s climate and developing climate models to predict future climate changes.

Climate studies are mainly based on energy, momentum, and mass balances to develop climate models. However, Earth’s climate is complex with lots of processes that expand over a large range of timescales. The climate models that include many detailed processes often result in a large number of adjustable parameters and tend to cause difficulty in understanding and accepting the models. Other ways to improve climate models and reduce the number of climate uncertainties is to add constraints to the climate system. This usually involves use of the second law of thermodynamics on entropy. Entropic aspects of the climate are not as well developed as those based on energy, momentum, and mass balances. In addition, the second law of thermodynamics is stated in the form of an inequality, which causes some difficulty in applications.

This paper will discuss some thermodynamic concepts and apply them to describe Earth’s climate. Chapter 2 is an introduction to thermodynamics and entropy using the approach of Born and Carathéodory. The Born-Carathéodory approach to thermodynamics uses a mathematical approach and avoids using detailed arguments of Carnot cycles. Chapter 3 introduces some of the basic elements of the climate system using thermodynamics. Chapter 4 discusses the big picture on how the climate system is driven and maintained by radiation exchanges with space and the entropy associated with these exchanges. Chapter 5 discusses the role of entropy due to different processes inside the climate system, especially due to turbulence. In addition, a hypothesis on the Maximum Entropy Production principle is introduced. Chapter 6 discusses a climate model by Garth Paltridge that uses the Maximum Entropy Production principle where he was able to reproduce the long-term mean of the present climate.
Chapter 2

Introduction to Thermodynamics and Entropy

The goal of this chapter is to develop the laws of thermodynamics from the point of view of Born and Carathéodory. This approach is based on ideas from everyday experience and some simply stated physical laws. In this development, ‘heat’ comes out of theory and ‘entropy’ comes out in a nice mathematical way.

We begin by establishing Carathéodory’s theorem, which is purely mathematical. This theorem will serve as a tool that implies the existence of the entropy function. This chapter relies on sources [2], [9], and [8].

Definition 1 A \textbf{one-form} \( \omega \) on \( \mathbb{R}^n \) is an expression with the general form

\[
\omega = f_1 dx_1 + f_2 dx_2 + \cdots + f_n dx_n
\]

where \( f_1, f_2, \ldots, f_n \) are smooth functions in \( \mathbb{R}^n \).

Definition 2 A one-form \( \omega \) is \textbf{exact} if there exists a continuously differentiable function \( f \) such that

\[
\omega = df = \frac{\partial f}{\partial x_1} dx_1 + \frac{\partial f}{\partial x_2} dx_2 + \cdots + \frac{\partial f}{\partial x_n} dx_n
\]

Integration of one-forms are line integrals. Some facts about the integration of one-forms are:

\textbf{Fact 1} If \( \omega = df \) is an exact one-form on an open subset \( U \subset \mathbb{R}^n \) and \( c : [a, b] \to U \) is a parameterized curve, then

\[
\int_c \omega = \int_c df = f(c(b)) - f(c(a)).
\]

This means the integral of an exact one-form from \( c(a) \) to \( c(b) \) is path independent.

\textbf{Fact 2} If \( \omega \) is exact and \( c \) is a closed curve, i.e. \( c(a) = c(b) \), then \( \int_c \omega = 0 \). This follows from Fact 1.

A conclusion that is important for thermodynamics is if \( \int_c \omega \neq 0 \) for some particular curve \( c \), then \( \omega \) is not exact. For one-forms that are not exact, the integral from \( c(a) \) to \( c(b) \) is path dependent.

Definition 3 A curve \( c \) that is continuous and piecewise differentiable is called a \textbf{null curve} of \( \omega \) if

\[
\int_c \omega = 0.
\]

A proof of the following theorem is given in [2].
Theorem 1 (Carathéodory’s Theorem) Let $\omega$ be a one-form such that for any point $p$ there are points arbitrarily close to $p$ which cannot be joined to $p$ by a null curve of $\omega$. Then there exists smooth functions $f$ and $g$ such that $\omega = fdg$.

The functions $f$ and $g$ are not unique for the following reason. If $g = H \circ G$ and $f = \frac{F}{H'(G)}$, where $H$ is any differentiable function of one variable with nowhere vanishing derivative and $H'(G) \neq 0$, then

$$fdg = \frac{F}{H'(G)}d(H \circ G)$$
$$= \frac{F}{H'(G)}H'(G)dG$$
$$= FdG.$$

However, it can be shown that if $f$ is given, then $g$ is unique up to an additive constant.

2.1 Born-Carathéodory Approach to Thermodynamics

The Born-Carathéodory approach to thermodynamics provides mathematical formalism for the theory. It is based on the ideas from everyday experience and simply stated physical laws. The theory of thermodynamics is formulated in terms of standard concepts of elementary mechanics. Then the laws are modified to include notions of heat and temperature. Using simply stated physical laws together with Carathéodory’s theorem lead to concepts of absolute temperature and entropy. We start by making some physical assumptions.

The first assumption is that a portion of the universe that we are interested in studying can be isolated from the rest of the universe. The isolated portion of the universe is called a system. The system can exist in various states which can be complicated and there are infinitely many states. Mathematically, a system is some differentiable manifold that represents some characteristics of a physical system. The states are variables which serve as coordinates of the system. We can specify various interactions that occur with the system and the rest of the universe.

The second assumption is that among all the possible states of a system, there is a prominent class of states called equilibrium states. If the rest of the universe was held constant, the system will pass through various states but tend to a definite equilibrium state. The equilibrium state is determined by the initial state of the system at the moment the interactions are held constant. The set of equilibrium states is modeled by a submanifold of $\mathbb{R}^N$. An example of a system in equilibrium is to consider a liquid in a closed container. If the liquid is not moving in any way (i.e. rotating, translating), has a constant density (so there is no net evaporation), has a constant temperature, and the volume of the container is fixed, then the system is most likely in thermodynamic equilibrium since the system’s mechanical, chemical,
or thermal attributes are not changing with time.

The following assumptions single out certain types of interactions. There are two special types of interactions, diathermal contact and adiabatic interactions. **Diathermal contact** or diabatic interaction is a special form of interaction between two systems where there is no observed macroscopic motion nor exchange of materials. Consider two original systems, System 1 and System 2, that combine to form a new system. If \( p_1 \) is the state of System 1 and \( p_2 \) is the state of System 2, then \( (p_1, p_2) \) is the state of the combined system. In diathermal contact, the equilibrium states of the combined system is a subset of the collection of pairs of the equilibrium states of the original two systems. In other words, if \( p_1 \) is an equilibrium state of System 1 and \( p_2 \) is an equilibrium state of System 2, when the two systems are brought into diathermal contact, then the combined system will tend to a definite equilibrium \( (q_1, q_2) \) where \( q_1 \) and \( q_2 \) are the new equilibrium states of System 1 and System 2, respectively. In this case, we say that System 1 in state \( q_1 \) is in thermal equilibrium with System 2 in state \( q_2 \).

It is observed that thermal equilibrium is an equivalence relation. Let \( p_1, p_2, \) and \( p_3 \) be the equilibrium states of System 1, System 2, and System 3, respectively. If System 1 and System 2 are brought in diathermal contact, then \( p_1 \) is in thermal equilibrium with \( p_2 \). Similarly, if System 2 and System 3 are brought in diathermal contact, then \( p_2 \) is in thermal equilibrium with \( p_3 \). This implies that the equilibrium states \( p_1 \) and \( p_3 \) of System 1 and System 3 are in thermal equilibrium. The equivalence class of all systems at thermal equilibrium is called an abstract temperature (this assumption is sometimes called the zeroth law of thermodynamics).

When describing a system, there are certain parameters that play an important role. For example, if the system is a container of gas, the total volume occupied and the total mass of each chemical component that make up the gas would be such parameters. These parameters are called configurational variables or extensive variables. Each system has \( N \) parameters defined on a set of its states called configurational variables. Specifically, the set of equilibrium states is modeled by a submanifold of \( \mathbb{R}^N \) for some \( N \) that depends on the system and has local coordinates \( (T, x_1, x_2, ..., x_n) \) where \( T \) represents the abstract temperature and \( x_1, x_2, ..., x_n \) are configurational variables. Configurational variables are additive and depend on the size of the system. Given \( k \) moles of a pure substance, we observe one mole of the substance that would be in equilibrium with \( k \) moles. If several phases of the substance are present, we assume the same percentage of each phase occur in the one mole sample as the \( k \) mole sample. For example, if \( u \) is the internal energy of one mole, then based on the assumptions made, the internal energy for \( k \) moles is \( U = ku \). Some examples of configurational variables are volume, mass, number of moles, and internal energy. Roughly speaking, if you have \( k \) times as much of the “same kind of stuff,” then each of the parameters listed would be \( k \) times as large. For contrast, there are intensive variables such as temperature, density, and pressure. Intensive variables take on the same value for one mole of substance as for \( k \) moles.
of the same substance. They are independent of the quantity of the material present in the system.

Another important class of interactions of the system with the rest of the universe is called **adiabatic interactions**. An interaction of the system with the rest of the universe is adiabatic if the equilibrium of the system is unchanged unless there is some change in the configurational variables. A physical interpretation of adiabatic interactions is that there is no heat exchanged between the system and the rest of the universe (e.g., a thermos bottle). If all interactions are adiabatic for a period of time, then the system is in an adiabatic enclosure.

A curve $\gamma$ joining two states $\sigma$ and $\sigma'$ while the system is in an adiabatic enclosure is called an adiabatic curve. The first law of thermodynamics is a generalization from experience which says that if a system in an adiabatic enclosure is brought from one state $\sigma$ to another state $\sigma'$ by applying external work, then the amount of work is always the same no matter how the work is applied. Therefore, there exists a function, called the internal energy function $U$ on the space of states such that

$$W = U(\sigma') - U(\sigma) \tag{2.1}$$

where $W$ is the work done on the system when bringing the system from state $\sigma$ to $\sigma'$ along any adiabatic curve. If a system is not adiabatically enclosed, then let the difference be denoted by $Q$,

$$Q = U(\sigma') - U(\sigma) - W. \tag{2.2}$$

We call $Q$ the heat transferred to the system. In this case, the heat supplied $Q$ and the work done $W$ depend on the process, not just the initial and final states $\sigma$ and $\sigma'$. In terms of one-forms, the **first law of thermodynamics** can also be written as

$$\delta Q = dU - \delta W \tag{2.3}$$

where $dU$ is an exact one-form, the differential of internal energy and $\delta W$ and $\delta Q$ are inexact one-forms of work and heat respectively.

The next idea is that of a reversible curve. A **reversible** path, $\gamma(t)$, is a curve on the manifold of the equilibrium states. In other words, for every time $t$, the state $\gamma(t)$ is “close” to an equilibrium state. For an intuitive meaning of reversibility, suppose there is a gas inside a container with a piston and the interaction is to change the volume of the gas by pulling out or pushing in the piston. If the gas is in an equilibrium state and we quickly push or pull the piston, the new state of the gas will not be in an equilibrium state. However, if we fix the position of the piston after the sudden movement, the gas will settle back into a new equilibrium state. To achieve a reversible path, we can push or pull the piston sufficiently slowly so that the gas is approximately in an equilibrium state the whole time. This process is called a **quasistatic** process and is a piecewise differentiable curve in state space. In the case of volume changes, we observe the existence of a pressure function $p$ so that the work
done on the system along any reversible curve is given by

\[ W = - \int_{\gamma} p \, dV. \]  

(2.4)

With work defined as equation (2.4), the first law of thermodynamics can be rewritten as

\[ \delta Q = dU + p \, dV. \]  

(2.5)

An adiabatic reversible path is therefore a null curve on a manifold of equilibrium states for \( \delta Q \).

Given a system in an adiabatic enclosure, there are certain types of work that can be done on the system such as violent shaking or stirring that is irreversible even after the system settles down to equilibrium. Irreversible meaning that one cannot get back to the initial state by any reversible adiabatic curve. This can happen at any equilibrium state and is the main idea of the second law of thermodynamics.

**Second law of thermodynamics:** Near any equilibrium state \( \sigma \) of any system, there exists arbitrarily close equilibrium states that cannot be joined to \( \sigma \) by reversible adiabatic curves.

This law says that near any point of the manifold of equilibrium states, there are arbitrarily close points that cannot be reached by null curves of \( \omega \). It follows from Carathéodory’s theorem that for any system, \( \delta Q = f \, dg \) for some function \( f \) and \( g \). Careful arguments show there exists a universal absolute temperature scale \( f = T \) determined up to a multiplicative constant. Fixing this constant determines a function \( g \) of Carathéodory’s theorem, which we will henceforth denote by the standard symbol \( S \). This function \( S \) on the set of equilibrium states is determined up to an additive constant for any system, and is called entropy. The heat one-form is given as

\[ \delta Q = T \, dS. \]  

(2.6)

If two equilibrium states \( \sigma_1 \) and \( \sigma_2 \) can be joined by a reversible adiabatic curve, then \( dS = 0 \), and \( S(\sigma_1) = S(\sigma_2) \). However, suppose we start with an equilibrium state \( \sigma_1 \) and perform an irreversible adiabatic process to end up at another equilibrium state \( \sigma_2 \), then the curve joining \( \sigma_1 \) to \( \sigma_2 \) might not lie in the submanifold of the equilibrium states even though the endpoints do. We cannot get back to the original state unless heat is taken out of the system. This leads to a stronger formulation of the second law of thermodynamics can be made from this which states:

**Stronger version:** If the equilibrium states \( \sigma_1 \) and \( \sigma_2 \) can be joined by an adia-
batic curve, a process leading from $\sigma_1$ to $\sigma_2$, then

$$S(\sigma_1) \leq S(\sigma_2)$$

(2.7)

i.e. entropy increases. $S(\sigma_1) = S(\sigma_2)$ if and only if $\sigma_1$ and $\sigma_2$ can be joined by a reversible adiabatic curve.

### 2.2 Interacting Systems Exchanging Entropy

The concept of entropy can be extended to open systems that exchange energy and matter. Suppose we have two systems in contact to build a larger system. Let $\sigma = (\sigma_1, \sigma_2)$, where $\sigma$ is an equilibrium state of the combined system and $\sigma_1$ and $\sigma_2$ are equilibrium states of the individual systems. Then we can write the total internal energy as the sum of its components

$$U(\sigma) = U(\sigma_1) + U(\sigma_2).$$

(2.8)

We make the physically reasonable assumption that the ‘interaction’ energy is negligible in comparison with the sum of the individual energies. Entropy for systems in contact is also additive, i.e.

$$S(\sigma) = S(\sigma_1) + S(\sigma_2).$$

(2.9)

Once an entropy function is defined on all states, the second law can be strengthened to say that if a system is placed in an adiabatic enclosure, the entropy of any state will not decrease as time evolves. Entropy will only increase unless the system is in equilibrium.

In physics, there are many conservation laws on physical quantities such as energy, momentum, and mass that have been established. However, the second law of thermodynamics regarding entropy is in the form of an inequality to which there is no corresponding conservation law [13]. There is an important characterization of equilibrium states for entropy called the maximum entropy principle which says:

among all states with a given internal energy the entropy increases monotonically until it reaches a maximum entropy at the state of thermodynamic equilibrium.

This is the basic underlying principle and there are variations of this principle that are useful in practice. The maximum entropy principle is used in various disciplines of science. In this thesis, we will apply this principle to the climate system. To see how the maximum entropy principle plays a role, we must discuss the basics of the Earth’s climate system.
Chapter 3

Elements of the Climate System

Earth’s climate is a complex system in which a wide variety of physical processes take place. The atmosphere plays a central role by exchanging energy with its surroundings. The transfers of energy maintain thermal equilibrium and determine the Earth’s climate.

The atmosphere consists of a mixture of ideal gases. Although the atmosphere mainly consists of molecular nitrogen and molecular oxygen by volume, the minor constituents such as carbon dioxide and water vapor are important in radiative and chemical processes. The Sun is the primary source of the forcing of the atmosphere, however, interactions with the land and the ocean are also important contributing sources.

Thermodynamic principles are essential for describing atmospheric processes. Understanding the climate system is important to developing models to predict climate patterns. Basic elements of the climate system such as radiation and atmospheric dynamics are discussed in this chapter. This chapter relies on the references [24] and [1].

3.1 Radiation

Atmospheric radiation involves the transfer of energy within the atmosphere by photons or electromagnetic waves. There is a large spectrum of electromagnetic waves classified by their wavelengths. In the order of increasing wavelengths, there are gamma rays, x-rays, ultraviolet, visible, infrared, microwave, radio waves, and long radio waves. Most of the radiation from the Sun, in terms of intensity, is in the visible range. The wavelengths of visible light (colors of the rainbow) lie between violet at about 0.4 µm and red at about 0.7 µm. Light with wavelengths shorter than violet is called ultraviolet radiation and light with wavelengths longer than red is called infrared radiation. The radiation that affects the climate system comes from the ultraviolet, visible, and infrared regions of the electromagnetic spectrum, but primarily from the latter two.

When light hits matter, the photons can reflect, pass through, or become absorbed depending on the medium. Light passes through materials that are transparent such as air and water. By contrast, light is absorbed by materials that are opaque such as the Earth’s surface. The ratio of reflected light to incident light is called albedo $A$. The Earth’s planetary albedo is taken to be about $A = 0.3$. The 30% of light that is reflected back to space is mainly by clouds and secondarily by ice and snow. The albedo of snow covered ice is close to $A = 1$, and the albedo of sea water is close

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1 It is partly for this reason that humans and other species evolved with the ability to see radiation within the “visible” range.
to $A = 0$. What happens to the 70% of solar photons that is not reflected back to space?

The remaining solar photons are mainly absorbed by the Earth’s surface. Over large timescales, it is assumed that the Earth’s atmosphere is in thermal equilibrium; the net energy gained must be zero. There are two types of radiative transfer that occur in the atmosphere. **Solar** or **shortwave radiation** is emitted by the Sun and corresponds to ultraviolet, visible, and near infrared wavelengths of $0.1 - 0.4 \mu m$. To balance the energy gained by solar radiation, the Earth’s atmosphere and surface emits **thermal** or **longwave radiation** to space and corresponds mainly to infrared and far infrared wavelengths of $4 - 100 \mu m$.

### 3.1.1 Black Body Radiation

We need to determine the relationship between heat and light. When light is absorbed by matter, the matter is heated. The reverse is also true, when matter is heated, the matter emits light. The temperature of an object determines the intensity of the radiation emitted at various wavelengths or frequencies of radiation.

A **black body** is an idealized body which absorbs all incident radiation. The theory of black body radiation is the foundation for describing thermal emission and is modeled by the energy emitted by an isolated cavity with uniform temperature. To maintain uniform temperature, a black body that absorbs radiant energy must also emit it. Black bodies have the following characteristics: the radiation of a black body is uniquely determined by the temperature of the emitter; for a given temperature, the radiant energy emitted is the maximum possible at all wavelengths; the radiation is isotropic.

The theory of black body radiation was developed by Planck in the early twentieth century. To develop the theory of black body radiation, Planck assumed that the energy $E$ of molecules go through discrete transitions that satisfy

$$\Delta E = \Delta n h\nu$$

where $n \in Z$, $h = 6.63 \times 10^{-34}$ J s is Planck’s constant, and $\nu$ is the frequency of electromagnetic radiation emitted or absorbed to reach a transition in energy $\Delta E$. The connection between wavelength $\lambda$ and frequency $\nu$ is

$$c = \lambda \nu$$

where $c = 3.00 \times 10^8$ m/s is the speed of light. Equation (3.1) gives a relationship between energy and light for a black body. The radiation emitted or absorbed by individual molecules is quantized in photons that carry energy in increments of $h\nu$.

Based on the energy relation of equation (3.1), Planck found the **spectral radiance** (power per unit area, per unit solid angle, per unit frequency) for a black body
at absolute temperature $T$ to be

$$B_\nu(T) = \frac{2h\nu^3}{c^2(e^{\hbar\nu/k_B T} - 1)} \quad (3.3)$$

where $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant. Equation (3.3) is known as the Planck function. The Planck function can also be written using wavelength instead of frequency by a change of variable using equation (3.2). The spectral radiance for a black body in terms of its wavelength is

$$B_\lambda(T) = \frac{2hc^2}{\lambda^5(e^{hc/\lambda k_B T} - 1)}. \quad (3.4)$$

In general, the spectral radiance depends on position and direction. However, since black body radiation is isotropic, the Planck function is independent of position and direction. If $B_\lambda(T)$ is integrated over all wavelengths, then the black body radiance (power per unit area, per unit solid angle) $B(T)$ is

$$B(T) = \int_0^\infty B_\lambda(T) \, d\lambda$$

By substitution, let $x = \frac{hc}{\lambda k_B T}$, so $dx = -\frac{hc}{x^2 k_B T} \, d\lambda$. Then the preceding equation becomes

$$B(T) = \frac{2k_B T^4}{h^3 c^2} \int_0^\infty \frac{x^3}{e^x - 1} \, dx$$

$$= \frac{2k_B T^4}{h^3 c^2} \left( \frac{\pi^4}{15} \right)$$

$$= \frac{\sigma T^4}{\pi} \quad (3.5)$$

where $\sigma = \frac{2k_B \pi^3}{15 hc c^2} = 5.67 \times 10^{-8}$ W/m$^2$K$^4$ is the Stefan-Boltzmann constant. The relationship between temperature and the irradiance (power emitted per unit area) of a black body is given by the Stefan-Boltzmann law. It is found by integrating equation (3.5) over all solid angles on a hemisphere

$$F = \int_0^{2\pi} \int_0^{\pi/2} B(T) \sin \theta \cos \theta d\theta d\phi = \pi B(T) = \sigma T^4. \quad (3.6)$$

The concept of a black body is an idealization. Real substances absorb and emit radiation at rates smaller than a black body. The spectral absorptance (or absorptivity) $a_\lambda$ is the ratio of intensity a substance absorbs to $B_\lambda(T)$. Similarly, the spectral emittance (or emissivity) $\epsilon_\lambda$ is the ratio of intensity emitted by a substance to $B_\lambda(T)$. Kirchoff’s law states that at a given temperature and wavelength, the
The spectral emittance of a body is the same as the spectral absorptance, i.e. \( \epsilon_\lambda = a_\lambda \).

The laws discussed so far are for a body with uniform temperature. The atmosphere does not have a uniform temperature, therefore it is not strictly under thermodynamic equilibrium. Under certain conditions, some portions of the atmosphere are said to be in **local thermodynamic equilibrium** (LTE) where the temperature is uniform and radiation is isotropic. At altitudes below 60 km, certain portions of the atmosphere satisfy LTE allowing the functions and laws established in the section to hold.

### 3.2 Basic Model

Using some of the concepts discussed so far, a simple estimate of the average emitting temperature of the Earth with a non-absorbing atmosphere can be made. At Earth’s mean distance from the Sun, the **total solar irradiance**, or solar power per unit area, is \( F_s = 1370 \text{ W/m}^2 \). Assume that the beams of solar radiation are parallel at the Earth. The Earth intercepts solar radiation of cross sectional area \( \pi r_E^2 \) where \( r_E \) is the radius of the Earth (see Figure 3.1). About \( A = 0.3 \) of the solar radiation is reflected back into space, which leaves \((1 - A)F_s\) of the incoming solar radiation to become absorbed by the Earth’s surface.

![Figure 3.1: Basic Model](image)

The average solar power per unit area absorbed by the Earth’s surface, \( F_0 \), is the ratio of the total energy that makes it to Earth over the surface area of the Earth, i.e.

\[
F_0 = \frac{(1 - A)F_s \pi r_E^2}{4\pi r_E^2} = \frac{(1 - A)F_s}{4} \approx 240 \text{ W/m}^2.
\]

Assume the Earth is in thermal equilibrium and emits as a black body with uniform temperature \( T_e \). To maintain thermal equilibrium, the Earth must emit longwave radiation to space at the same rate as the incoming shortwave radiation. Since the Earth emits as a black body, power is emitted isotropically and the Stefan-Boltzmann law, equation (3.6), can be applied. The total power emitted over the surface area of
the Earth is $4\pi r_E^2 \sigma T_e^4$. Balancing the incoming and outgoing power gives

$$
(1 - A) F_s \pi r_E^2 = 4\pi r_E^2 \sigma T_e^4 \Rightarrow T_e = \left( \frac{(1 - A) F_s}{4} \right)^{1/4}.
$$

(3.8)

Substituting the values of $A$ and $F_s$, the effective emitting temperature of the Earth comes out to be $T_e = 255$ K or roughly $-2/3^\circ$ F. This is too cold and not a good model since the global mean surface temperature is about $T_s = 288$ K. The model is missing the effect of radiation trapping.

### 3.3 The Greenhouse Effect

The difference between $T_e$ and $T_s$ comes from how the Earth’s atmosphere processes shortwave and longwave radiation. The atmosphere is nearly transparent to solar radiation and almost opaque to infrared radiation. Solar radiation passes freely to the Earth’s surface, but infrared radiation emitted by the Earth’s surface gets absorbed by overlying air. The infrared radiation re-emits half upwards toward space and half downwards toward the Earth’s surface. Infrared radiation gets absorbed by more overlying air and re-emits in a similar fashion. This process repeats until the longwave radiation eventually radiates beyond all absorbing components of the atmosphere and is sent out to space. The low absorption of solar radiation and high absorption of infrared radiation is called the **greenhouse effect**. The greenhouse effect raises the temperature of the Earth, insulating it and allowing for life.

The opacity of the atmospheric layers to longwave radiation involves the molecular components that make up the atmosphere. The atmosphere is composed of various gases, mostly molecular nitrogen ($N_2$) (78% by volume), molecular oxygen ($O_2$) (21% by volume), water vapor ($H_2O$), carbon dioxide ($CO_2$), methane ($CH_4$), ozone ($O_3$), and other minor gases that make up the remaining 1% of the atmosphere. Gases that mainly absorb longwave radiation are water vapor, clouds, methane, and carbon dioxide. Ozone, nitrous oxide ($NO_2$), and fluorinated gases also absorb longwave radiation, but are not abundant in the atmosphere. The gases that absorb longwave radiation, but allow solar radiation to pass relatively freely are referred to as **greenhouse gases**.

To illustrate the role of the greenhouse effect on Earth’s climate, a second basic model is introduced. Consider a layer of atmosphere with uniform temperature $T_a$ and a ground layer with uniform temperature $T_g$ (see Figure 3.2). Assume the atmosphere transmits a fraction of incident shortwave radiation $T_{sw}$ and transmits a fraction of incident longwave radiation $T_{lw}$. These fractions are called **transmittances**.

From the first model, we know the average unreflected solar irradiance absorbed at the top of the atmosphere is $F_0 \approx 240\text{W/m}^2$. Of this amount, an irradiance of $T_{sw} F_0$ is absorbed by the ground. Assuming that the ground emits as a black body, it emits an upward irradiance of longwave radiation of $F_g = \sigma T_g^4$ (by Stefan-Boltzmann’s law).
The portion of $F_g$ that reaches the top of the atmosphere is $T_{lw}F_g$. The atmosphere is not a black body, but emits irradiances $F_a$ upwards and downwards. Kirchoff’s law is used to find the relation between $F_a$ and the transmittance. At thermal equilibrium, the ratio of the actual emitted irradiance $F_a$ to the irradiance emitted by a black body is equal to the fraction of incident light on a body that is absorbed, i.e.

$$\frac{F_a}{\sigma T_a^4} = 1 - T_{lw} \Rightarrow F_a = (1 - T_{lw})\sigma T_a^4. \quad (3.9)$$

Assume the system is in radiative equilibrium, the amount of incoming radiation is equal to the amount of outgoing radiation everywhere. The balance equations for above the atmosphere and between the atmosphere and the ground, respectively, are

$$F_0 = F_a + T_{lw}F_g \quad (3.10)$$
$$T_{sw}F_0 + F_a = F_g. \quad (3.11)$$

The unknown quantities in the system of equations are $F_a$ and $F_g$. Solving for $F_a$ in equations (3.10) and (3.11) gives

$$F_a = F_0 - T_{lw}F_g \quad (3.12)$$
$$F_a = F_g - T_{sw}F_0 \quad (3.13)$$

Equating (3.12) and (3.13) and solving for $F_g$ yields

$$F_0 - T_{lw}F_g = F_g - T_{sw}F_0 \Rightarrow F_g = \frac{F_0(1 + T_{sw})}{1 + T_{lw}}. \quad (3.14)$$
To find $F_a$, plug equation (3.14) into equation (3.12) or (3.13). This gives

$$F_a = F_0 \left( 1 - \frac{T_{sw} T_{lw}}{1 + T_{lw}} \right).$$

(3.15)

Use Stefan-Boltzmann’s law to obtain $T_g$ and $T_a$

$$\sigma T_g^4 = \frac{F_0(1 + T_{sw})}{1 + T_{lw}} \Rightarrow T_g = \left( \frac{F_0(1 + T_{sw})}{\sigma(1 + T_{lw})} \right)^{1/4}$$

(3.16)

$$F_a = (1 - T_{lw}) \sigma T_a^4 = F_0 \left( 1 - \frac{T_{sw} T_{lw}}{1 + T_{lw}} \right) \Rightarrow T_a = \left( \frac{F_0(1 - T_{sw} T_{lw})}{\sigma(1 - T_{lw})} \right)^{1/4}.$$  

(3.17)

Plugging in values of $F_0 = 240$ W/m$^2$, $T_{lw} = 0.2$ (weak transmittance and strong absorptance of longwave radiation), and $T_{sw} = 0.9$ (strong transmittance and weak absorptance of shortwave radiation) into equations (3.16) and (3.17) results in the temperature of the ground to be $T_g \approx 286$K and the temperature of the atmosphere to be $T_a \approx 245$K. The temperature of the ground $T_g$ is closer to the observed value of $T_s = 288$K.

This model is a simple illustration of the greenhouse effect. The surface temperature $T_g$ increased to a closer observed value because there is less absorption (or greater transmittance) of shortwave radiation than there is for longwave radiation. The quantities of transmittance was set so the layer of atmosphere is able to transmit shortwave radiation easily, but has a tendency to trap longwave radiation.

### 3.4 Atmospheric Motion

Under radiative equilibrium, the first law of thermodynamics reduces to a balance equation between radiative transfers of energy. This simple balance works for an atmosphere at rest, but breaks down for an atmosphere in motion since heat can transfer mechanically by air movement. The Earth is unevenly heated by the Sun. Lower latitudes near the equator have the most exposure annually to solar radiation while higher latitudes near the poles have the least exposure. Taking the seasons into account further complicates the distribution of radiant energy. The result is a horizontal transfer of heat from the equator to the poles by atmospheric circulation and is often referred to as the general circulation.

The atmosphere is a fluid system. Modeling fluid systems is complex because of a fluid’s ability to redistribute mass and constituents into an infinite number of configurations as it moves through its surroundings. This section introduces the basics of fluid dynamics that governs the atmospheric flows. Assume the flow of fluid is continuous.
3.4.1 Material Derivative

There are two frameworks for studying fluid motion, Eulerian and Lagrangian. The Eulerian description of fluid motion uses fixed inertial coordinates and follows Newton’s laws of motion. A fluid is modeled as a vector field where we fix a point \((x, y, z)\) and watch how the velocity changes at that point. The Lagrangian description follows an individual parcel of fluid with an arbitrary shape. The laws of physics are applied to represent the fluid’s behavior in terms of the collective properties of material elements that make up the fluid. The Lagrangian framework represents the thermal, mechanical, and chemical histories of the parcel along with its position and distortion as it moves through its surrounding. There is a fundamental kinematic restraint that connects the Lagrangian and Eulerian descriptions: the field property at a given location and time must equal the property possessed by the material element occupying that position at that instant.

To transform from the Lagrangian description to the Eulerian description, the Lagrangian derivative involving conservation laws must be expressed in terms of field properties. Let \(F = F(t, x(t), y(t), z(t))\) where \(F\) is some physical quantity of interest. Differentiating \(F\) with respect to time \(t\) gives

\[
\frac{d}{dt}F(t, x(t), y(t), z(t)) = \frac{\partial F}{\partial t} + \frac{\partial F}{\partial x} \frac{dx}{dt} + \frac{\partial F}{\partial y} \frac{dy}{dt} + \frac{\partial F}{\partial z} \frac{dz}{dt}
\]

(3.18)

\[
= \frac{\partial F}{\partial t} + \mathbf{v} \cdot \nabla F
\]

(3.19)

where \(\mathbf{v} = \left(\frac{dx}{dt}, \frac{dy}{dt}, \frac{dz}{dt}\right)\) is the velocity field. The first term on the right side of equation (3.19) is the rate of change of \(F\) at a fixed location \((x, y, z)\), and the second term represents the change of \(F\) following the motion of the parcel to positions of different field values. Equation (3.19) is called the material derivative.

**Definition 4** The operator

\[
\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla
\]

(3.20)

is called the **material derivative** or **advective derivative**.

The material derivative \(\frac{DF}{Dt}\) represents the rate of change of \(F\), not at a fixed point, but following the motion of the fluid whose velocity field is \(\mathbf{v}\).

The changes of \(F\) described by the material derivative, equation (3.20), apply to an infinitesimal material element. Now consider changes for a finite material volume \(V(t)\) containing a fixed collection of matter. For this, Leibniz’s rule for differentiating an integral is applied.

**Theorem 2 (Leibniz’s rule)** Let \(F(x, y, z, t)\) be a function on the region of flow.
Let $V(t)$ be the domain of a parcel of fluid that moves with the flow. Then

$$
\frac{d}{dt} \iiint_{V(t)} F(x,y,z,t) \, dx \, dy \, dz = \iiint_{\partial V(t)} \mathbf{F} \cdot \mathbf{n} \, dS + \iiint_{V(t)} \frac{\partial F}{\partial t} \, dx \, dy \, dz
$$

$$
= \iiint_{V(t)} \frac{\partial F}{\partial t} + \nabla \cdot (\mathbf{F} \mathbf{v}) \, dx \, dy \, dz \tag{3.21}
$$

where $\mathbf{v}$ is the velocity of the fluid, $\mathbf{n}$ is the outward unit normal, and $dS$ is the element of area.

The two versions of the formula are equivalent by the divergence theorem. For simplicity, a proof of the one dimensional version is shown.

**Theorem 3** If $f(x,t)$, $g(t)$, and $h(t)$ are continuously differentiable, then

$$
\frac{d}{dt} \int_{g(t)}^{h(t)} f(x,t) \, dx = [f(h(t),t) h'(t) - f(g(t),t) g'(t)] + \int_{g(t)}^{h(t)} \frac{\partial f(x,t)}{\partial t} \, dx \tag{3.22}
$$

**Proof.** Let $u = g(t)$, $v = h(t)$, and $F(t) = \int_{u}^{v} f(x,t) \, dx = G(u,v,t)$.

Then

$$
F'(t) = \frac{d}{dt} F(t) = \frac{d}{dt} G(u,v,t)
$$

$$
= \frac{\partial G}{\partial u} \frac{du}{dt} + \frac{\partial G}{\partial v} \frac{dv}{dt} + \frac{\partial G}{\partial t} \frac{dt}{dt}
$$

$$
= \left( \frac{\partial}{\partial u} \int_{u}^{v} f(x,t) \, dx \right) g'(t) + \left( \frac{\partial}{\partial v} \int_{u}^{v} f(x,t) \, dx \right) h'(t) + \int_{u}^{v} \frac{\partial f(x,t)}{\partial t} \, dx
$$

$$
= \frac{\partial}{\partial u} [F(v,t) - F(u,t)] g'(t) + \frac{\partial}{\partial v} [F(v,t) - F(u,t)] h'(t) + \int_{u}^{v} \frac{\partial f(x,t)}{\partial t} \, dx
$$

$$
= -f(u,t)g'(t) + f(v,t)h'(t) + \int_{u}^{v} \frac{\partial f(x,t)}{\partial t} \, dx
$$

$$
= f(h(t),t)h'(t) - f(g(t),t)g'(t) + \int_{u}^{v} \frac{\partial f(x,t)}{\partial t} \, dx
$$

The proof for the three dimensional version is given in the Appendix.

The three dimensional case of Leibniz’s rule is often referred to as Reynolds’ transport theorem in fluid mechanics. It relates the time rate of change of some property of a finite body of fluid to the corresponding field variable and the velocity field.
3.4.2 Conservation of Mass

Imagine following a parcel of fluid (or air) occupying a volume $V(t)$ at time $t$. Let $\rho = \rho(x, y, z, t)$ be the density of fluid. The density $\rho$ is a function of position $(x, y, z)$ and time $t$. The mass $M$ of the parcel of air is given by

$$M = \iiint_{V(t)} \rho(x, y, z, t) \, dx \, dy \, dz. \tag{3.23}$$

Let $\mathbf{v} = \mathbf{v}(t) = \frac{dx}{dt}$ be the velocity of the fluid, where $\mathbf{x} = (x(t), y(t), z(t))$. To conserve mass, we need $\frac{dM}{dt} = 0$. This leads to

$$\frac{dM}{dt} = 0 \Rightarrow \frac{d}{dt} \iiint_{V(t)} \rho(x, y, z, t) \, dx \, dy \, dz = 0. \tag{3.24}$$

Applying Leibniz’s rule, the preceding equation becomes

$$\iiint_{V(t)} \left( \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) \right) \, dV = 0. \tag{3.25}$$

Equation (3.25) must hold for any material volume $V(t)$. This implies

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0. \tag{3.26}$$

Equation (3.26) is called the continuity equation or mass conservation law for an individual parcel of air. The term $\nabla \cdot (\rho \mathbf{v})$ can be expanded and the continuity equation can also be written as

$$\frac{\partial \rho}{\partial t} + \nabla \rho \cdot \mathbf{v} + \rho \nabla \cdot \mathbf{v} = 0. \tag{3.27}$$

The continuity equation can also be written using the material derivative as

$$0 = \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = \left[ \frac{\partial \rho}{\partial t} + \nabla \rho \cdot \mathbf{v} \right] + \nabla \cdot \mathbf{v} \rho = \frac{D\rho}{Dt} + (\nabla \cdot \mathbf{v}) \rho$$

$$\Rightarrow \frac{D\rho}{Dt} = -(\nabla \cdot \mathbf{v}) \rho \tag{3.28}$$

If $\nabla \cdot \mathbf{v} = 0$, the fluid is said to be incompressible and $\frac{D\rho}{Dt} = 0$.

Combining some of the concepts from this section gives the following lemma.

**Lemma 1** Let $F$ be a smooth scalar function and $\rho$ is the density of a fluid with
velocity $\mathbf{v}$. Then

$$\frac{d}{dt} \iiint_{V(t)} \rho F \, dV = \iiint_{V(t)} \rho \frac{DF}{Dt} \, dV$$  \hspace{1cm} (3.29)$$

where $V(t)$ is a finite material volume containing a fixed collection of matter.

**Proof.**

\[
\begin{align*}
\frac{d}{dt} \iiint_{V(t)} \rho F \, dV &= \iiint_{V(t)} \frac{\partial (\rho F)}{\partial t} \, dV + \nabla \cdot (F(\rho \mathbf{v})) \, dV \\
&= \iiint_{V(t)} \left[ \frac{\partial \rho}{\partial t} F + \frac{\partial F}{\partial t} \rho + (\nabla F) \cdot \mathbf{v} + (\nabla \cdot \mathbf{v}) F \right] \, dV \\
&= 0, \text{ by continuity equation} \\
&= \iiint_{V(t)} \rho \frac{DF}{Dt} \, dV
\end{align*}
\]

There is another equation called the **Navier-Stokes equation**, which is a conservation of momentum equation for fluids. The Navier-Stokes equation can be derived using the material derivative. Without going through the derivation, the Navier-Stokes equation for compressible fluid flow in an inertial frame is

$$\frac{D\mathbf{v}}{Dt} = g\mathbf{k} - \frac{1}{\rho} \nabla p + \mathbf{F}_{\text{visc}}$$  \hspace{1cm} (3.30)$$

where $g$ represents the gravity, $\mathbf{k}$ is the unit vertical vector $(0, 0, 1)$, $p$ represents the pressure forces acting on a parcel of fluid, and $\mathbf{F}_{\text{visc}}$ represents the viscous force exerted on the parcel of fluid at location $\mathbf{x}$. Equation (3.30) says that the momentum of a parcel of fluid according to the resultant force exerted on it by gravity, pressure gradient, and viscous (frictional) drag.

The equations of motion provide a starting point for dynamic modeling. These equations give a system of partial differential equations. The material derivative makes the governing equations nonlinear and require initial conditions of the state of the atmosphere and boundary conditions of properties along the physical borders. This causes difficulty in forecasting the behavior of the atmosphere.
Chapter 4
Entropy of Solar and Infrared Radiation

The Earth’s climate has changed over the industrial period as seen by increasing global surface temperatures and rising sea levels. The main cause of this is due to greenhouse gases. Global climate change can lead to uninhabitable conditions causing threats to human health or extinction, increasing numbers and severity of extreme weather events, and changes in water and ecosystems. Climate models that accurately predict future climate changes can give an effective strategy to protect Earth’s unique climate that allows for life.

Climate models are primarily based on the principles of energy, momentum, and mass balances. The usual approach to climate modeling is to build a model based on these principles and examine its sensitivity to parameter changes. Many detailed interactions of processes that are relevant to the climate system span over a large range of space and time scales. This increases the number of adjustable parameters and causes the model to become very sensitive to parameter changes [26].

Another approach to studying Earth’s climate is to add thermodynamic constraints on the system. Generally, this type of approach uses the second law of thermodynamics regarding entropy. The maximum entropy production principle (see Section 2.2) is often used to explain some behaviors of the climate system without knowing details of the dynamics within the system. Entropic aspects of the climate system are not as well developed as the models based on energy momentum, and mass balances, but are attractive because of their simplicity [25]. This thesis focuses more on this type of approach especially the maximum entropy production principle.

Most processes in the climate system are irreversible so they produce entropy. For irreversible processes, the system goes in and out of thermodynamic equilibrium with its surroundings and cannot be reversed entirely without leaving a net influence on the system or its surroundings. A small perturbation to the system can trigger a spontaneous process or reaction. Processes involving friction such as turbulent mixing and transformations of phase when different phases are not in equilibrium are irreversible processes that naturally take place in the climate system. The Earth system as a whole is driven and maintained by radiation exchanges. The Earth absorbs shortwave radiation, converts it into other energy forms by irreversible processes (creating entropy), and reradiates longwave radiation back to space. Under steady state conditions, we can compare the rate of incoming and outgoing entropy production of the Earth.

4.1 Entropy Budget of the Earth as a Whole

This section relies on references [22], [25], and [26]. Recall that for an isolated system, the second law of thermodynamics says $dS \geq 0$. This implies that energy changes from a higher to a lower level of availability. For an increase in entropy of a system,
there is a decrease in available energy. The second law of thermodynamics can also be extended to open systems that exchange energy and matter with its surroundings. The climate system is taken to be closed to material exchange, but open to radiation exchange with space. With this open system, a balance equation for entropy is defined for the climate system.

The total rate of entropy production for the Earth’s climate system $dS/dt$ is measured by the rate of entropy transferred into the system through the top of the atmosphere $dS_1/dt$ and the rate of entropy produced inside the system by irreversible processes $dS_2/dt$. $dS_1/dt$ can be positive, negative, or zero depending on the direction of flow. Let the positive direction be the entropy flowing into the system. The total rate of entropy production for the Earth is given by the balance equation for entropy

$$\frac{dS}{dt} = \frac{dS_1}{dt} + \frac{dS_2}{dt}, \quad \frac{dS_2}{dt} \geq 0 \quad (4.1)$$

By the second law of thermodynamics, $dS_2/dt$ is always nonnegative and equals zero for reversible processes.

Over a sufficiently long period of time, the climate system is in a steady state. The steady state assumption allows the total rate of entropy production to be negligible, i.e. $dS/dt = 0$. Using the steady state assumption on equation (4.1) leads to

$$\frac{dS_2}{dt} = -\frac{dS_1}{dt}, \quad (4.2)$$

which says that the Earth’s internal entropy production can be measured by the net entropy flowing out of the system through the top of the atmosphere. Radiative equilibrium also holds under a steady state; the amount of energy absorbed by solar radiation is balanced by the amount of energy emitted by infrared radiation. The definition of the rate of entropy change is

$$\frac{dS}{dt} = \frac{\delta q}{T}, \quad (4.3)$$

where $\delta q$ is the inexact one-form of the rate of heat production and $T$ is the absolute temperature. Equation (4.3) says that when heat is supplied quasi-statically to the system with an absolute temperature $T$, then the rate of entropy increases by $\delta q/T$. When heat is extracted from the system, then the entropy decreases proportionally. Thus for an open system that exchanges energy with its surroundings, the entropy can increase or decrease depending on the direction of heat exchange [17]. This is not a violation of the second law of thermodynamics since the entropy increase in the surrounding area is larger. The law of entropy increase applies to an isolated system, or in our case the whole system ($dS/dt$). Equation (4.3) can be used to compare the entropy exchanged between the Earth and space.

To compare the entropy exchanged, assume the Sun and the Earth emit as black
bodies. The Sun emits at a surface temperature of $T_{\text{Sun}} \approx 5800$ K, while the Earth emits at an average temperature of $T_{\text{Earth}} \approx 288$ K. In thermal equilibrium, the rate of heat transfer $\delta q$ to and from Earth are equal. The rate of entropy production of the Earth is

$$\frac{dS_{\text{Earth}}}{dt} = \frac{\delta q}{T_{\text{Earth}}}$$

and the incoming rate of entropy from the Sun is

$$\frac{dS_{\text{Sun}}}{dt} = \frac{\delta q}{T_{\text{Sun}}}.$$  (4.5)

The rate of incoming and outgoing heat exchanged $\delta q$ are the same, however, the associated temperatures are different. Since $T_{\text{Sun}} >> T_{\text{Earth}}$, we can compare the rate of entropy exchanged

$$\frac{dS_{\text{Sun}}}{dt} = \frac{\delta q}{T_{\text{Sun}}} \ll \frac{\delta q}{T_{\text{Earth}}} = \frac{dS_{\text{Earth}}}{dt}.$$  (4.6)

The incoming rate of entropy from the Sun going to Earth is much smaller than the outgoing rate of entropy from the Earth to space resulting in a negative net entropy flux.

To further understand the entropy imbalance, we can compare the quality of short-wave solar radiation to longwave (or terrestrial) radiation emitted by the Earth. Incoming shortwave radiation travels with a maximum wavelength of $\lambda_{\text{max,sw}} \approx 0.47 \mu m$ while outgoing longwave radiation travels with a maximum wavelength of $\lambda_{\text{max,lw}} \approx 10 \mu m$. By Planck’s equation, $E = h\nu$ (see Section 3.1.1) for each photon. This means that a photon that travels with a higher frequency carries a greater amount of energy. Since wavelength and frequency are inversely related, solar radiation has a higher frequency than terrestrial radiation. So for a fixed amount of energy, the Earth must emit far more photons with maximum intensity to match the maximum intensity of one solar photon. Thus, we can view incoming solar radiation as more organized than the longwave radiation Earth sends out to space.

The thermodynamic definition of entropy, equation (4.3), was developed in 1865 by Rudolf Clausius. This definition of entropy was proposed when studying systems that do not include radiation. Radiation has unique properties that are distinct from ordinary matter. Electromagnetic waves can travel through empty space without any need for a material medium. For example, solar radiation propagates through empty space from the Sun to the Earth.

Unlike molecules or atoms, photons of radiation have the property of wave-particle duality and this complicates the thermodynamic treatment of radiation. There is some disagreement in the scientific literature even about the basic relationship, (4.3). Some researchers (see e.g. [26]) argue for a factor of $4/3$ on the left side of (4.3) based on the following reasoning.
To understand this argument, first note that in the context of radiation of the term \( Q \) in (4.3) plays a role of energy flux \( U \), rather than only heat. So equations (4.4) and (4.5) would be more properly be expressed by replacing the heat terms by total energy transferred. Second, we note that radiation pressure is the pressure exerted on any surface that is exposed to electromagnetic radiation. For black body radiation, Maxwell’s radiation pressure is given by,

\[
p = \frac{u}{3}
\]

where \( u \) is the energy density per unit volume of radiation. Note that \( U \) denotes the total internal energy, so \( U = uV \). We mention also that \( u \) depends only on the temperature \( T \) of the emitting black body. The derivation starts with Clausius’s definition of entropy

\[
dS = \frac{\delta Q}{T} = \frac{dU + p \, dV}{T} \quad \text{by first law of thermodynamics}
\]

\[
= \frac{u \, dV + (u/3) \, dV}{T} \quad \text{by Maxwell’s radiation pressure}
\]

\[
= \frac{4}{3} \frac{u \, dV}{T}.
\]

(4.8)

In this context \( du \) is the radiation energy density flux one-form. The \( 4/3 \) factor would be needed when the radiation exerts pressure that causes a change in volume. It is not needed for radiation emitted into free space that performs no work. We adopt the point of view that the factor \( 4/3 \) is not needed for our context. In our case, we compare the entropies of ingoing and outgoing, each in equilibrium, at the top of the atmosphere. Once radiation exerts pressure on a physical object, that radiation is no longer in equilibrium. For extensive discussions and debates on this topic, see [12], [17], [26] and the references therein.
Chapter 5

Entropy in the Climate System

The Earth’s atmosphere is a fluid system that transports heat from hot regions to cold regions of the Earth. The Sun heats the Earth mainly around the equatorial region. Some of the heat energy becomes stored as mechanical energy, which is a source for kinetic energy. The kinetic energy creates motions in the atmosphere and ocean transferring heat poleward (or horizontally) from the warm equator to the cool poles. As an overall picture, there is a circulation of energy from the hot Sun, through the Earth’s atmosphere and oceans, and back out to cold space (see Figure 5.1). Describing the Earth’s system in this manner allows us to view Earth as an engine that carries heat between two reservoirs. This chapter discusses the role of entropy production in the climate system reviewed by [17].

To study heat flow and entropy production, we start by modeling the heat circulation of the climate system as described by Figure 5.1. Consider two large thermal reservoirs with different temperatures (see Figure 5.2). The hot reservoir has temperature \( T_h \) that can represent the hot equatorial region of the Earth. The cold reservoir has temperature \( T_c \) that can represent the cold polar region. The two reservoirs are connected so that heat can flow from the hot reservoir to the cold reservoir by passing through a small system. The small system can be a solid system or a fluid system. The solid system can represent the Earth’s surface and the fluid system can represent the Earth’s atmosphere or oceans. Using this model, as illustrated by Figures 5.1 and 5.2, we can study the rate of entropy production.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig5.1.png}
\caption{Energy flows from the hot Sun to Earth, circulates through the Earth’s atmosphere and oceans, and is ejected into cold space.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{fig5.2.png}
\caption{A model representation of Figure 5.1.}
\end{figure}

From equation (4.3), the rate of entropy production of a system relies on the rate of heat transfer along with the absolute temperature of the system. The rate of heat transfer varies depending on the method of heat transfer. Heat can be transferred by radiation, conduction, or convection. The topic of radiation was covered in Chapter
3. Heat conduction is the transfer of internal energy by microscopic diffusion and collisions of particles within the body. In general, conduction is a slow process. The effectiveness of heat transfer by conduction depends on the material of the body. Solid bodies are better heat conductors than fluid bodies. Convection is the transfer of heat from one place to another by the movement of fluids. In this case, the rate of entropy production is affected by the method of heat transfer and material of the body absorbing the heat.

5.1 Entropy Production in Solid Systems

First, let us examine the rate of entropy production when the system is a solid. Heat is transferred by conduction through the solid system. In a steady state, the incoming and outgoing heat fluxes are the same; therefore the heat flux has a linear relationship with the temperature. To calculate the total rate of entropy production of the entire system, we examine the rate of entropy production of each chamber (hot reservoir, cold reservoir, and solid system). Let $F$ be the heat flux through the solid system. The rate of entropy that leaves the hot reservoir is $\frac{dS_2}{dt} = -\frac{F}{T_h}$ and the rate at which entropy enters the cold reservoir is $\frac{dS_1}{dt} = \frac{F}{T_c}$. The negative sign on $\frac{dS_2}{dt}$ indicates that heat is leaving the hot reservoir. Since the small system is in a steady state, $\frac{dS_3}{dt} = 0$. The total rate of entropy production of the whole system $\frac{dS_{\text{whole}}}{dt}$ is

$$\frac{dS_{\text{whole}}}{dt} = \frac{dS_1}{dt} + \frac{dS_2}{dt} + \frac{dS_3}{dt} = \frac{F}{T_c} - \frac{F}{T_h} + 0 = \frac{T_h - T_c}{T_h T_c} F \geq 0. \quad (5.1)$$

From the second law of thermodynamics, the heat flux is positive, i.e. $F \geq 0$, since heat flows from hot regions to cold regions. Equation (5.1) represents the rate of entropy production of the entire system by the irreversible heat transport from hot to cold. The heat transport is irreversible because there is no heat stored as mechanical energy inside the small system. With the small system in a steady state, the amount of entropy produced inside the system is discharged into its surroundings.

Over a long period of time, i.e. $t \to \infty$, the temperature difference of the entire system is negligible. The temperature of the whole system is homogeneous and is considered to be in a state of thermodynamic equilibrium where the entropy production for the whole system is at a maximum. With this viewpoint, the whole system is in a nonequilibrium state and tries to reach an equilibrium state by transporting heat through the small system.

5.2 Generation and Dissipation of Work

The heat conduction process described in the last section is an irreversible process. Now consider transferring heat from the hot reservoir to the cold reservoir in a reversible manner. Let the small system be a fluid system with low viscosity (such as
water or air) that does not yet experience turbulence. Turbulence is random, unpredictable fluid flow. For a reversible process, some of the heat entering the small system from the hot reservoir can be converted into mechanical energy or work $W$ (for example through a “Carnot Cycle” [9]). The outgoing heat flux from the system into the cold reservoir is $F_{\text{out}} = F_{\text{in}} - W$ and can be less than the incoming heat flux.

The general circulation of the atmosphere uses mechanical energy in the form of kinetic energy to transport heat from the equator to the poles. In the hemisphere, the circulation is split into three cells: the Hadley cell, the Ferrell cell, and the Polar cell. The Hadley cell is a thermally direct circulation from the equator to the tropics. Warm air rises near the equator and travels towards the poles. As the warm air approaches the subtropical latitude, it is cooled and sinks. The Ferrel cell is a thermally indirect circulation located in the mid-latitudes in which cold air is forced to rise. Relatively cold air rises at the higher mid-latitude and travels towards the lower mid-latitude where there is a sink of relatively warm air. The Polar cell is similar to the Hadley cell but located in the high latitudes. Warm air rises in the higher mid-latitude and travels to the pole where it is cooled and sinks leading to a thermally direct circulation. The large-scale advection due to winds of the general circulation is considered a reversible process. Reversing the motion can reverse the heat transport.

The total rate of entropy production for the whole system undergoing a reversible process is

$$\frac{dS_{\text{whole}}}{dt} = \frac{F_{\text{out}}}{T_c} - \frac{F_{\text{in}}}{T_h} = \frac{F_{\text{in}} - W}{T_c} - \frac{F_{\text{in}}}{T_h} \geq 0 \quad (5.2)$$

Equation (5.2) is still nonnegative by the second law of thermodynamics. Solving inequality (5.2) for $W$, the maximum possible work done by the system during the heat transport is

$$W \leq \frac{T_h - T_c}{T_h} F_{\text{in}} = \left(1 - \frac{T_c}{T_h}\right) F_{\text{in}}. \quad (5.3)$$

The inequality above shows that the maximum possible work is proportional to the incoming heat flux and the temperature difference. The amount of work possible by the system is bounded above by $F_{\text{in}}$, the incoming heat flux.

The climate system, or any real system, cannot produce the maximum amount of work thermodynamically allowed by equation (5.3) because there are many irreversible processes that take place. Irreversible processes such as heat conduction and friction do not generate work. This allows heat to discharge into its surroundings and increases the rate of entropy production. The discharged heat reduces the net heat absorbed by the system and in turn decreases the amount of work possible by the system. The mechanical energy available in the small system can also be used to generate heat irreversibly. For example, kinetic energy (a form of mechanical energy) causes the friction between material surfaces or viscosity in fluids to create heat. The heat
created further increases the rate of entropy production. Extra terms must be added to the rate of entropy production, equation (5.2), when considering the irreversible conversions of mechanical energy into heat energy. However, in a steady state, all the mechanical energy available eventually dissipates into heat energy resulting in the same rate of entropy production as in the case of the solid system, equation (5.1).

5.3 Entropy Production in Fluid Systems

Now consider the small system to be a fluid with low viscosity that can experience turbulence. The fluid is heated from the bottom and cooled at the top (see Figure 5.2). Bénard studied the convection of this system in 1901. To describe what happens in the system, imagine a parcel of fluid inside the small system. Near the bottom of the system, the parcel is heated; the volume of the parcel expands and the density decreases causing it to rise. Towards the top, the parcel is cooled; the volume of the parcel contracts and the density increases causing it to sink. Initially, during the process, energy is stored in the form of potential energy by the differential heating. As the cooler fluid at the top becomes denser than the warmer fluid underneath, the system becomes gravitationally unstable. When the fluid is no longer stable to small perturbations, convective motion or turbulence tends to develop.

During turbulence, some of the stored potential energy converts to kinetic energy to physically move the fluid. The motion of the fluid itself creates heat energy and increases the total heat flux $F$. To illustrate, now consider the same parcel moving through a turbulent environment. Turbulent forces are exerted onto the parcel causing it to continuously deform. If the parcel was partitioned into layers, then the layer that is in direct contact of the force moves the most. Adjacent layers of the parcel slide into the direction of the force in decreasing amounts proportional to the distance away from the location of the source. The layers move with different velocities creating friction between the fluid layers, and in turn produces heat which dissipates into its surrounding. This dissipation of heat from the motion of the fluid is referred to as viscous dissipation.

The dynamic equation and conservation equations involving turbulence are nonlinear. The nonlinearity comes from converting potential energy to kinetic energy to viscous dissipation. Finding analytic solutions for nonlinear processes is difficult. However, we know from before that when the overall system is in a steady state, the rate of energy entering and leaving the system is equal. This means that the generation of potential energy is balanced by the viscous dissipation and the rate of entropy production is the same as the case of the solid system, equation (5.1).

A general expression can be found for the rate of entropy production of a fluid system with an arbitrary shape. The arbitrary shape of the fluid allows us to generalize the whole system to the fluid system and its surrounding (see Figure 5.3). However, one could imagine Figure 5.2 as an example. For a turbulent fluid system that exchanges heat with its surroundings, define a positive heat flux $F$ to point out of the
fluid system. The rate of entropy production for a turbulent fluid system is the rate of entropy production inside the system, \( \frac{dS_{\text{system}}}{dt} \) and its surrounding \( \frac{dS_{\text{surr}}}{dt} \), i.e.

\[
\frac{dS_{\text{turb}}}{dt} = \frac{dS_{\text{whole}}}{dt} = \frac{dS_{\text{system}}}{dt} + \frac{dS_{\text{surr}}}{dt}
\]  \( (5.4) \)

where \( \frac{dS_{\text{turb}}}{dt} \) represents the rate of entropy production of a system undergoing turbulence. The term \( \frac{dS_{\text{turb}}}{dt} \) is used to distinguish the case of a fluid system that experiences turbulence from the other systems discussed previously.

Let \( s \) represent the entropy per unit mass, \( \rho \) is the density of the fluid, \( V \) is the volume of the fluid system, and \( A \) is the surface boundary of the fluid system. Then equation (5.4) becomes

\[
\frac{dS_{\text{turb}}}{dt} = \frac{d}{dt} \left[ \int_V \rho s \, dV \right] + \int_A \frac{F}{T} \, dA.
\]  \( (5.5) \)

The first term on the right side of equation (5.5) is the time rate of change of entropy of the fluid system. The integrand, \( \rho s \), represents the entropy per unit volume. Leibniz’s rule is applied to the first term on the right side of equation (5.5). Although the volume \( V \) and surface area \( A \) are fixed, the application of Leibniz’s rule is valid because the interior points of the fluid system are changing with respect to time. The second term on the right side of equation (5.5) represents the rate of entropy entering or leaving the system at the boundary. Applying Leibniz’s rule to (5.5) gives

Figure 5.3: Generalized model of a turbulent fluid system.
\[
\frac{dS_{\text{turb}}}{dt} = \int_V \left[ \frac{\partial(\rho s)}{\partial t} + \nabla \cdot (\rho s \mathbf{v}) \right] dV + \int_A \frac{F}{T} dA
\]

\[
= \int_V \left[ \rho \left( \frac{\partial s}{\partial t} + \mathbf{v} \cdot \nabla s \right) + s \left( \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) \right) \right] dV + \int_A \frac{F}{T} dA
\]

\[
= \int_V \rho \left( \frac{\partial s}{\partial t} + \mathbf{v} \cdot \nabla s \right) dV + \int_A \frac{F}{T} dA
\]

\[
= \int_V \rho \frac{Ds}{Dt} dV + \int_A \frac{F}{T} dA.
\]  

(5.6)

We can use the following thermodynamic relation, which combines the first and second laws of thermodynamics. In the Lagrangian framework,

\[
\frac{ds}{dt} = \frac{\delta q}{T} = \frac{1}{T} \left( \frac{du}{dt} + p \frac{dV}{dt} \right).
\]  

(5.7)

To transform equation (5.7) to the Eulerian framework,

\[
\frac{Ds}{Dt} = \frac{1}{T} \left( \frac{Du}{Dt} + p \frac{DV}{Dt} \right).
\]  

(5.8)

Since we are working with a unit of mass,

\[
V = \frac{m}{\rho} = \frac{1}{\rho}.
\]  

(5.9)

Continuing on finding the rate of entropy production in a fluid system, use equations (5.8) and (5.9) in the first term of equation (5.6).
\[
\frac{dS_{\text{turb}}}{dt} = \int_V \frac{\rho}{T} \left(\frac{Du}{Dt} + p \frac{D(1/\rho)}{Dt}\right) dV + \int_A F dA \\
= \int_V \frac{\rho}{T} \left[\frac{\partial u}{\partial t} + \mathbf{v} \cdot \nabla u + p \left(-\frac{1}{\rho^2} \frac{D\rho}{Dt}\right)\right] dV + \int_A F dA \\
\text{use continuity equation (3.28)} \\
= \int_V \frac{\rho}{T} \left[\frac{\partial u}{\partial t} + \mathbf{v} \cdot \nabla u - \frac{p}{\rho^2} (-\rho \nabla \cdot \mathbf{v})\right] dV + \int_A F dA \\
= \int_V \frac{\rho}{T} \left[\frac{\partial u}{\partial t} + \mathbf{v} \cdot \nabla u + \frac{p}{\rho} (\nabla \cdot \mathbf{v})\right] dV + \int_A F dA \\
= \int_V \frac{1}{T} \left[\rho \frac{\partial u}{\partial t} + \rho \mathbf{v} \cdot \nabla u + p \nabla \cdot \mathbf{v}\right] dV + \int_A F dA \\
= \int_V \frac{1}{T} \left[\frac{\partial (\rho u)}{\partial t} + \nabla \cdot (\rho u \mathbf{v}) + p \nabla \cdot \mathbf{v}\right] + \int_A F dA, \\
\text{where the last line uses Lemma 1 from Chapter 3. Now we can apply the following} \\
\text{relation of a unit of energy, } u = c_V T, \text{ where } c_V \text{ is the specific heat when the} \\
\text{volume is fixed. The specific heat is the amount of heat per unit mass required to raise} \\
\text{the temperature by one degree Celsius. Using this relation, the preceding equation} \\
\text{becomes} \\
\frac{dS_{\text{turb}}}{dt} = \int_V \frac{1}{T} \left[\frac{\partial (\rho c_V T)}{\partial t} + \nabla \cdot (\rho c_V T \mathbf{v}) + p \nabla \cdot \mathbf{v}\right] dV + \int_A F dA. \quad (5.10)
\]

The first term on the right side of equation (5.10) can be rewritten using the heat conduction equation. The heat conduction equation expresses the law of the conservation of energy for a fluid (see [5] for details). The heat conduction equation is
\[
\frac{\partial (\rho c_V T)}{\partial t} + \nabla \cdot (\rho c_V T \mathbf{v}) = -p \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{F} + \Phi, \quad (5.11)
\]
where \(\mathbf{F}\) is the rate of heat conduction and \(\Phi\) is the rate of viscous dissipation. The heat conduction equation expresses the rate of change of internal energy as the rate at which work is done on the fluid system by compression, the rate of heat conduction, and the rate of viscous dissipation. Moving \(p \nabla \cdot \mathbf{v}\) to the left side of equation (5.11) and substituting it into equation (5.10) gives
\[
\frac{dS_{\text{turb}}}{dt} = \int_V \frac{1}{T} (-\nabla \cdot \mathbf{F} + \Phi) dV + \int_A F dA \\
= -\int_V \frac{1}{T} (\nabla \cdot \mathbf{F}) dV + \int_V \frac{\Phi}{T} dV + \int_A F dA. \quad (5.12)
\]
The divergence theorem is used to transform the surface area integral into a volume
integral. The divergence theorem is applied to the product of the scalar function \(1/T\) and the vector field \(\mathbf{F}\).

\[
\int_V \left[ \mathbf{F} \cdot \left( \nabla \frac{1}{T} \right) + \frac{1}{T} (\nabla \cdot \mathbf{F}) \right] \, dV = \int_A \frac{1}{T} \mathbf{F} \cdot \mathbf{n} \, dA
\]

\[\Rightarrow \int_V \mathbf{F} \cdot \left( \nabla \frac{1}{T} \right) \, dV = \int_A \frac{1}{T} \mathbf{F} \cdot \mathbf{n} \, dA - \int_V \frac{1}{T} (\nabla \cdot \mathbf{F}) \, dV \quad (5.13)\]

Substituting equation (5.13) into (5.12) where \(F = \mathbf{F} \cdot \mathbf{n}\), we found another way to express the rate of entropy production of a turbulent fluid system (5.10) as

\[
\frac{dS_{\text{turb}}}{dt} = \int_V \mathbf{F} \cdot \nabla \left( \frac{1}{T} \right) \, dV + \int_V \Phi \, dV. \quad (5.14)
\]

The rate of entropy production for a fluid experiencing turbulence depends on the rate of heat conduction and the rate of viscous dissipation. The first term on the right side of equation (5.14) represents the rate of entropy production by transferring heat from hot regions to cold regions by conduction. The second term represents the rate of entropy production by viscous dissipation (frictional dissipation of heat caused by kinetic energy in the fluid). For the climate system, the heat flux \(\mathbf{F}\) includes irreversible processes such as latent heat transport (energy released due to phase changes of water), radiative transport, and sensible heat transport (thermal conduction).

If the system as a whole is in a steady state, then the rate of entropy production inside the system is discharged into its surrounding. The entropy produced inside the system is released into the surrounding system through the boundary so the net rate of change of entropy of the fluid system is negligible, i.e. \(dS_{\text{system}}/dt = 0\). For the steady state case, the rate of entropy production follows from equation (5.5) that

\[
\frac{dS_{\text{turb}}}{dt} = \frac{dS_{\text{system}}}{dt} + \frac{dS_{\text{surr}}}{dt} = \int_A \frac{F}{T} \, dA. \quad (5.15)
\]

The entropy of the surrounding system increases by the irreversible processes inside the fluid system. In the case of heat conduction, equation (5.15) of the turbulent fluid system is analogous to the solid system, equation (5.1).

Equations (5.14) and (5.15) represent the rate of entropy production for turbulent fluid systems. Equation (5.14) is considered a local expression because it is described by small scale dissipative processes in the system. On the other hand, equation (5.15) is a global expression because it is described by the total rate of all the small scale processes from equation (5.14). The local and global expressions have been shown to be equivalent. The steady state case, equation (5.15), along with a maximum principle is used to estimate the rate of entropy production of the climate system.
5.4 Maximum Entropy Production

The maximum entropy production (MEP) principle is a hypothesis that says: a non-linear system with many degrees of freedom for dynamic motion tends to a state with maximum entropy production among all other possible states. This principle has been applied in many fields including biology, chemistry, and physics. For this thesis, we are interested in the application of the MEP principle to turbulent fluid systems. The MEP principle applies to turbulent fluid systems because the process is nonlinear. It follows from equation (5.14) that the rate of entropy production

\[
\frac{dS_{\text{turb}}}{dt} = \int_V \mathbf{F} \cdot \nabla \left( \frac{1}{T} \right) \, dV + \int_V \frac{\Phi}{T} \, dV = \text{maximum}. \tag{5.16}
\]

If the fluid system is in a steady state, then from equation (5.15), the rate of entropy production of the fluid system is unchanged and the rate of entropy production is

\[
\frac{dS_{\text{turb}}}{dt} = \int_A \frac{F}{T} \, dA = \text{maximum}. \tag{5.17}
\]

The MEP principle on turbulent fluid systems, equations (5.16) and (5.17), is a hypothesis that is tested by showing agreement in observational and experimental evidence. This hypothesis has been tested on the climate system.
In 1975, Garth Paltridge proposed that the mean state of the present climate is reproducible by using the MEP principle. This was a significant departure from the usual approach, based on various conservation laws. At the time, it was assumed that a solution would be found by adding enough details to significant weather or climate processes. Using the MEP principle along with basic descriptions of atmospheric and oceanic dynamics, Paltridge was able to reproduce the latitudinal mean temperature, cloud cover, and meridional energy flux of the entire globe. This chapter follows the work done by Paltridge [19] and [20].

To start, Paltridge hypothesized that there are sufficient degrees of freedom in the climate system that can be governed by an extremum principle. Success in this approach would allow accurate climate predictions without complete descriptions of climate processes. However, the challenge is finding which quantity to maximize or minimize. There had been various suggestions as to which quantity in the climate system to optimize. Lorenz (1960) proposed to maximize the ratio of kinetic energy production to solar energy input [14]. Dutton (1973) suggested minimizing entropic energy, which is measured by the difference of entropy in equilibrium state and the entropy in any natural state in the atmosphere [6]. The equilibrium state of entropy is the entropy present when the atmosphere in a motionless, hydrostatic (proportional change of pressure to height in the atmosphere), and isothermal state. To find a quantity to optimize, Paltridge developed a box model of the entire globe.

A simple ten-box model of the entire globe was made. The globe was cut into equal surface areas on its latitude and an energy balance condition was assumed for each box (see Figure 6.1). Each box has energy fluxes represented in terms of surface temperature $T$, cloud cover $\theta$, and the meridional energy flux $F_m$. The meridional energy flux is the transfer of energy coming into a box from the adjacent boxes (see Figure 6.2).

Figure 6.1: Box model for the entire globe.
Each individual box has two energy balance equations, one for the atmosphere and one for the ocean. The energy balance equation for a box of atmosphere is

\[
\frac{R_0 - g R_0 (1 - \theta) - d R_0 \theta}{\xi} - \left[ \epsilon \sigma T^4 (1 - \theta) + G \sigma T^4 (1 - \theta) + f \epsilon' \sigma T^4 \theta \right] + F_m = 0,
\]

where \( R_0 \) is the solar irradiance, \( g \) is the albedo of the cloud free portion of the atmosphere, \( d \) is the albedo for the cloud covered portion of the atmosphere, \( \xi \) is the ratio of the actual surface area to the projected surface area as seen from the Sun, \( \epsilon \) is a fraction related to the width of the window region of the black body spectrum where direct radiation exchange between Earth’s surface and space is possible, \( G \) is a fraction of the longwave loss of the cloud free atmosphere to space as a function of surface black body emission, \( f \) is the fraction by which black body radiation from clouds is reduced due to their lower temperature, and \( \epsilon' \) is a constant related to the width of the window region of the infrared spectrum above most of the atmospheric water vapor. The first term in the bracket represents the net shortwave flux \( F_{\downarrow S} \) into the top of the atmosphere of the box. The second term in the bracket represents the net longwave flux from the atmosphere to space.

The energy balance equation for an ocean box is

\[
\frac{R_0 - g R_0 (1 - \theta) - (d + a) R_0 \theta - R_0 m}{\xi} - \left[ \epsilon \sigma T^4 - f \epsilon' \sigma T^4 \theta \right] - (L E + H) + F_{m,o} = 0,
\]

where \( a \) takes into account the extra shortwave absorption by liquid water in clouds and \( m \) the extra shortwave absorption by water vapor in the atmosphere. The first term in the bracket represents the net shortwave flux into the surface. The second term in the brackets represent the net longwave flux from the surface into the atmo-
The third term, $LE + H$, represents the ocean to atmosphere flux of latent and sensible heat. The last term, $F_{m,o}$, represents the meridional heat flux of the ocean part only.

The terms associated with the longwave fluxes use the Stefan-Boltzmann law for black body radiation. The Earth does not emit as a black body so using the Stefan-Boltzmann law is arguable, but the assumption is necessary for any box model of the atmosphere. Assuming the Earth emits as a black body is the simplest assumption. The parameters ($R_0, g, d, \xi, \epsilon, G, f, \epsilon, a, m$) in the balance equations are fixed values based on empirical evidence and theoretical calculations. Each individual box results in two energy balance equations with three unknowns, $T$, $\theta$, and $LE + H$.

To resolve the issue, a constraint was added. Paltridge suggested that the constraint was to maximize the rate of entropy production of the planet. From the model, the maximum rate of entropy production of the planet is calculated as the sum of the contributions from each box.

$$\frac{dS_I}{dt} = \sum_{i=1}^{10} \frac{F_{\uparrow L,i} - F_{\downarrow S,i}}{T_{a,i}} = \text{maximum} \quad (6.3)$$

d$S_I/dt$ represents the rate of internal entropy production. For the $i^{th}$ box, $F_{\downarrow S,i}$ represents the net shortwave flux into the top of the atmosphere, $F_{\uparrow L,i}$ represents the net longwave flux out through the top of the atmosphere, and $T_{a,i}$ represents the temperature of the top of the atmosphere. The rate of entropy production for the boxes near the hot equatorial region is negative since there is more incoming solar radiation. To balance this, the rate of entropy production of the boxes near the cold polar regions is positive since there is less incoming solar radiation. The overall value of equation (6.3) is positive because the mean temperature of the polar region is less than the mean temperature of the equatorial region.

The net flow of radiant energy at the top of the atmosphere, $F_{\uparrow L,i} - F_{\downarrow S,i}$, is a function of cloud cover and surface temperature. However, $\theta$ and $T$ are functions of the distribution $F_m$. The meridional energy fluxes are the fundamental unknowns. The model was designed to choose a unique set of values for $F_m$ that maximizes $dS_I/dt$ and satisfies the energy balance equations over the whole globe. The set $F_m$ also requires values that are close to the observed values. Finding such a set would lead to a maximum entropy production. Once all the meridional energy fluxes are specified for each box, $F_{\downarrow S,i}$, $F_{\uparrow L,i}$, $T_{a,i}$, and ultimately $dS_I/dt$ can be maximized. The values of $F_m$ that maximizes equation (6.3) were calculated using the simplex method of Nelder and Mead. The latent and sensible heat flux, $LE + H$, is a function of $T$ and $\theta$. The value of $LE + H$ was maximized by fixing $F_m$ and eliminating $\theta$ by combining equations (6.1) and (6.2). The maximum value was found by plotting $LE + H$ as a function of $T$ and the maximum lies inside the range of when $\theta \in [0, 1]$.

Paltridge found incredible results (see Figure 6.3) when maximizing equation (6.3) despite the simple treatments used in the model. Figure 6.3 shows the latitudinal distribution of temperature, cloud cover, and meridional heat flux. The solid line
represents the predicted values and the dashed line represents the observed values. The inaccuracies in the polar regions can be fixed by fine tuning the parameters in that region. Average values in the polar zones are hard to define since it covers a large range of latitude and solar angle. In addition, there is a sharp jump in albedo at the polar ice caps.

### 6.1 Turbulence Model

It was shown in [17] that the MEP of the turbulent fluid model in Chapter 5, equations (5.16) and (5.17), corresponds to that of Paltridge, equation (6.3). The steady state for the turbulent fluid model, equation (5.17), matches Paltridge’s hypothesis on using a state of maximum entropy production to reproduce the long-term mean of the climate. The basic model from Chapter 5 (Figure 5.2) is not equivalent to the box model of Paltridge. To match the two models, the model in Chapter 5 requires two turbulent fluid systems, one for the atmosphere and one for the ocean. This is done because the surroundings for the two systems are different. The energy fluxes affecting the atmosphere from space and the ocean/ground are different from the energy fluxes affecting the ocean from the atmosphere. The absorption and scattering processes in the atmosphere changes the energy flux that is absorbed by the ocean.

Extending equation (5.15), to the climate system in a steady state, the rate of entropy production that can experience turbulence is equal to the rate of entropy dissipated into its surrounding.
\[
\frac{dS_{\text{turb}}}{dt} = \frac{dS_{\text{turb},a}}{dt} + \frac{dS_{\text{turb},o}}{dt} = \int_A \frac{F}{T} \, dA + \int_0 \frac{F}{T} \, dA
\]
\[
= \int_A \left[ \frac{F_{lw}(\text{TOA}) - F_{sw}(\text{TOA})}{T_a} \right] - \left[ F_{lw}(0) - F_{sw}(0) \right] \, dA + \int_A \frac{F_{lw}(0) - F_{sw}(0)}{T_s} \, dA \quad (6.4)
\]

\[
\frac{dS_{\text{turb},a}}{dt} \text{ and } \frac{dS_{\text{turb},o}}{dt} \text{ are the discharge rates of entropy from the atmosphere and from the ocean, respectively. } T_a \text{ represents the temperature of the atmosphere and } T_s \text{ is the temperature of the ocean/ground. } F_{\text{sw}}(0) > 0 \text{ represents the net shortwave flux at the surface, and } F_{lw}(0) > 0 \text{ represents the net longwave flux at the surface. The minus sign denotes the direction of the flux points inwards towards the system.}
\]

The first term of equation (6.4) represents the rate of entropy discharged from the atmosphere into its surroundings (space and ocean/ground). The second term represents the rate of entropy discharged from the ocean/ground into the atmosphere. After rearranging the terms of equation (6.4), we see that the first term of equation (6.5) is the continuous form of the constraint made by Paltridge, equation (6.3), and represents the rate of entropy production from the horizontal heat transfer \( F_m \) due to turbulence. The second term of equation (6.5) represents the rate of entropy production from the vertical heat transfer due to turbulence (mainly known as convection, \( F_c = F_{lw}(0) - F_{lw}(0) \)). This term was not used in Paltridge’s original paper [19], but was made a maximum in a later paper [20]. The energy fluxes in equation (6.5) depend on the meridional heat flux \( F_m \) for the first term and the convective heat flux \( F_c \) for the second term.

In 1978, Paltridge extended the model to three dimensions [20]. He divided the world into 400 boxes of equal surface area. The parameters were adjusted to use satellite data. In addition, the horizontal energy fluxes were adjusted where oceanic energy flows were not allowed on continental areas. The results from the model matched observed quantities to a high degree of accuracy.

The MEP principle on the climate system gave credible results in predicting climate behavior. If one can accept this as a general principle that governs the climate system, then it can perhaps be used to predict climate change with fewer detailed analysis of the internal workings of the system.

### 6.2 Entropy Budget Model

So far, the maximized rate of entropy production has been associated only with turbulent dissipation in the atmosphere and oceans. Paltridge ascribed equation (6.3) as the total rate of entropy production for the whole planet [19], [20]. This was misleading to many researchers since the main source of entropy production is
due to the absorption of shortwave radiation in the atmosphere and surface. A large portion of the entropy production was left out when maximizing the rate of entropy production, yet Paltridge was able to reproduce accurate results.

The reason for leaving out a large source of entropy production while obtaining accurate results involves the linearity of radiation processes. The absorption of radiation is essentially a linear process. In turn, the rate of entropy production associated with the absorption of radiation is also linear. The MEP principle is conjectured only to apply to the entropy production rate due to nonlinear processes. The rate of entropy production associated with the absorption of radiation is therefore not expected to be part of the maximization process. Only the rate of entropy production due to turbulent dissipation tends to be a maximum due to its nonlinearity.

The difference between linear and nonlinear models is in the proportionality parameters. If the parameter is a constant, then the model is linear. However, if the parameter depends on unknown variables, then the model is nonlinear. For example, the specific heat capacity at constant volume, $c_V$, is a state variable that depends on pressure and temperature. This would lead to a nonlinear model, however, for the range of pressure and temperature relevant to the atmosphere, $c_V$ is viewed a constant. Then the internal energy for a unit of mass given in Chapter 4, $u = c_V T$ has a linear relationship since $c_V$ is constant.

The total rate of entropy production of the Earth can be found using rough values of various climate processes. This is useful to see the entropy contribution from different sources. A box model is used to represent the vertical energy fluxes, see Figure 6.4. The Earth receives solar radiation from the Sun with a temperature $T_{\text{Sun}} \approx 5800$ K and emits longwave radiation with the temperature of the atmosphere $T_a$. The rate of entropy production of the surrounding system (space) increases by

$$\frac{dS_{\text{surr}}}{dt} = \int_A \left( \frac{F_{lw}(\text{TOA})}{T_a} - \frac{F_{sw}(\text{TOA})}{T_{\text{Sun}}} \right) dA,$$

where $F_{lw}(\text{TOA})$ is the net rate of emission of longwave radiation per unit surface area at the top of the atmosphere, and $F_{sw}(\text{TOA})$ is the net rate of absorption of shortwave radiation per unit surface area at the top of the atmosphere. The long-term mean entropy production for the Earth is constant in a steady state, so

$$\frac{dS_{\text{system}}}{dt} = 0.$$

Then the rate of entropy production in the whole universe due to all irreversible processes of the Earth’s climate system is

$$\frac{dS_{\text{whole}}}{dt} = \frac{dS_{\text{system}}}{dt} + \frac{dS_{\text{surr}}}{dt} = \int_A \left( \frac{F_{lw}(\text{TOA})}{T_a} - \frac{F_{sw}(\text{TOA})}{T_{\text{Sun}}} \right) dA.$$
Equation (6.8) can be broken down into the sum of its contributions, i.e.

\[
\frac{dS_{\text{whole}}}{dt} = \frac{dS_{\text{turb}}}{dt} + \frac{dS_{\text{abs(sw,s)}}}{dt} + \frac{dS_{\text{abs(sw,a)}}}{dt} + \frac{dS_{\text{abs(lw,a)}}}{dt}.
\] (6.9)

d\!S_{\text{turb}}/dt is given by Equation (6.5). The rest of the terms follow from Section 5.1 for solid systems since each process is irreversible. The rate of entropy production due to the absorption of shortwave radiation at the Earth’s surface is

\[
\frac{dS_{\text{abs(sw,s)}}}{dt} = \int_A \left( \frac{1}{T_s} - \frac{1}{T_{\text{Sun}}} \right) F_{\text{sw}}(0) \, dA.
\] (6.10)

The rate of entropy production due to the absorption of shortwave radiation in the atmosphere is

\[
\frac{dS_{\text{abs(sw,a)}}}{dt} = \int_A \left( \frac{1}{T_a} - \frac{1}{T_{\text{Sun}}} \right) \left[ F_{\text{sw}}(\text{TOA}) - F_{\text{sw}}(0) \right] \, dA.
\] (6.11)

The rate of entropy production due to the absorption of longwave radiation in the atmosphere is

\[
\frac{dS_{\text{abs(lw,a)}}}{dt} = \int_A \left( \frac{1}{T_a} - \frac{1}{T_s} \right) F_{\text{lw}}(0) \, dA.
\] (6.12)

A vertical box model with rough values of temperatures and energy fluxes (in W/m\(^2\)) are given in Figure 6.4. The energy flux measurements are based from [15]
and [3]. Since this is a vertical box model, the horizontal contribution of rate of entropy production from turbulence (first term of equation (6.5)) is zero and there is only convection transport $F_c = 102 \text{ W/m}^2$. The shortwave energy flux at the top of the atmosphere is $F_{sw}(\text{TOA}) = 240 \text{ W/m}^2$. The shortwave energy flux absorbed at the surface is $F_{sw}(0) = 142 \text{ W/m}^2$. The net longwave energy flux at the surface is $F_{lw}(0) = 40 \text{ W/m}^2$. The temperature of the Sun, atmosphere, and Earth’s surface is $T_{\text{Sun}} \approx 5800 \text{ K}$, $T_a \approx 255 \text{ K}$, and $T_s \approx 288 \text{ K}$, respectively. The rate of entropy production of the whole universe (the whole box model) is

$$
\frac{dS_{\text{whole}}}{dt} = \left( \frac{F_{lw}(\text{TOA})}{T_a} - \frac{F_{sw}(\text{TOA})}{T_{\text{Sun}}} \right) = \left( \frac{1}{T_a} - \frac{1}{T_{\text{Sun}}} \right) 240 = 0.9 \frac{\text{W}}{\text{K m}^2}.
$$

(6.13)

The entropy production from each component is

$$
\frac{dS_{\text{whole}}}{dt} = \frac{dS_{\text{turb}}}{dt} + \frac{dS_{\text{abs}(sw,s)}}{dt} + \frac{dS_{\text{abs}(sw,a)}}{dt} + \frac{dS_{\text{abs}(lw,a)}}{dt}
$$

$$
= \left( \frac{1}{T_a} - \frac{1}{T_s} \right) 102 + \left( \frac{1}{T_s} - \frac{1}{T_{\text{Sun}}} \right) 142 + \left( \frac{1}{T_a} - \frac{1}{T_{\text{Sun}}} \right) 98 + \left( \frac{1}{T_a} - \frac{1}{T_s} \right) 40
$$

$$
= 0.046 \frac{\text{W}}{\text{K m}^2} + 0.469 \frac{\text{W}}{\text{K m}^2} + 0.367 \frac{\text{W}}{\text{K m}^2} + 0.018 \frac{\text{W}}{\text{K m}^2}.
$$

The entropy production from the absorption of shortwave radiation accounts for 93% of the total entropy production of the whole system. The entropy production from convection only accounts for 5% of the total entropy production. Although the rate of entropy production due to turbulence is very small compared to that of radiation, it is this small rate that tends to be a maximum in the climate system.
Chapter 7

Conclusion

This paper reviewed thermodynamic properties and applied them to the climate system. The second law of thermodynamics is a fundamental principle for which there is no corresponding conservation law. Earth’s radiation exchange with space drives and maintains almost all the processes within the Earth system [13]. The long-term mean exchange of incoming solar radiation and outgoing longwave radiation are the same, but the associated entropy fluxes are different. According to [22], the outgoing entropy associated with longwave radiation is about 22 times larger than the incoming entropy associated with solar radiation resulting in a negative net entropy flux. This provides a measure of the overall activities within the Earth's system including oceanic, atmospheric, and biological processes.

A general expression was found for the rate of entropy production for fluids experiencing turbulence. The MEP principle was applied to turbulent fluid systems since it is a nonlinear system and tested on the climate system. The model produced accurate predictions of the long-term mean of the present global climate, but it does not prove that the Earth’s climate system transports heat to achieve a state of MEP [17]. However, the MEP hypothesis has shown consistency on several types of turbulent fluid systems in nature such as the Rayleigh-Bénard convection and shear turbulence. It has also shown consistency when tested on climate systems of other planets and an Earth made of purely mantle material.

Lorenz [14] suggested that the Earth’s atmosphere operates in a way to generate available potential energy at a maximum possible rate. The available potential energy is defined as the maximum possible amount of potential energy available for kinetic energy. There was a discrepancy in his results, as he did not account for direct waste of energy by the irreversible process of latent heat transport. However, it has been shown that Lorenz’s hypothesis of maximum generation of available potential energy is identical to the MEP hypothesis. Ozawa et al qualitatively discusses a possible mechanism by which a turbulent fluid system self adjusts to a state of maximum generation of available potential energy, or MEP [17].

The study of atmospheric dynamics involving entropy is relatively new. The results tend to support the hypothesis of maximum entropy production. Entropy production of Earth’s climate involves many dynamic and thermodynamic processes, and the MEP principle provides a general insight on the overall configuration.
Bibliography


Appendix

Summary of Vector Calculus

1. Divergence Theorem. Let \( V \) be a three dimensional Jordan region and let \( \partial V \) be a smooth boundary surface of \( V \) with a positive (outward) orientation. If \( \mathbf{F} : V \to \mathbb{R}^3 \) is \( C^1 \) on \( V \), then

\[
\iint_{\partial V} \mathbf{F} \cdot \mathbf{n} \, dS = \iiint_V \nabla \cdot \mathbf{F} \, dV. \tag{1}
\]

2. Product rule for divergence. Let \( f : \mathbb{R}^3 \to \mathbb{R} \) and \( \mathbf{v} : \mathbb{R}^3 \to \mathbb{R}^3 \) be differentiable. Then

\[
\nabla \cdot (f \mathbf{v}) = \nabla f \cdot \mathbf{v} + f(\nabla \cdot \mathbf{v}). \tag{2}
\]

Leibniz’s Rule for Three Dimensions

As a reference, see [7]. Consider a fluid flowing through a region of space. Let \( F(x, y, z, t) \) be a function of position and time on the region of flow and let \( V_t \) be the domain of a parcel of fluid that moves with the flow.

**Theorem** Let \( \mathbf{u} \in C \) be the initial position and \( \mathbf{x} \in V_t \) be the moving point such that for each \( t, \phi_t : C \to V_t \). The domains \( C \) and \( V_t \) are Jordan regions. The map \((\mathbf{u}, t) \to \phi_t(\mathbf{u})\) is one-to-one and continuously differentiable. Then

\[
\frac{d}{dt} \iint_{V_t} F(x, y, z, t) \, dx \, dy \, dz = \iint_{\partial V_t} F \mathbf{v} \cdot \mathbf{n} \, dS + \iiint_{V_t} \frac{\partial F}{\partial t} \, dx \, dy \, dz
\]

\[
= \iiint_{V_t} \frac{\partial F}{\partial t} + \nabla \cdot (F \mathbf{v}) \, dx \, dy \, dz \tag{3}
\]

where \( \mathbf{v} \) is the velocity of the fluid, \( \mathbf{n} \) is the outward unit normal, and \( dS \) is the element of area.

**Proof.** Using index notation for coordinates, let \( \mathbf{u} = (u^1, u^2, u^3) \) be the initial position, \( \mathbf{x} = (x^1, x^2, x^3) \) be the moving point, and \( \mathbf{v} = (v^1, v^2, v^3) = \dot{\mathbf{x}} = (\dot{x}^1, \dot{x}^2, \dot{x}^3) \) be the velocity of the fluid. The dot denotes \( \partial/\partial t \).

Discussion: The proof of Leibniz’s rule relies on a change of variable. We have a domain \( C \) in \( \mathbf{u} \)-space, and for each \( t, \phi_t : C \to V_t \) of \( C \) into \( \mathbf{x} \)-space. The domain \( V_t \) has a fixed volume, but the interior points are moving with time. Both domains \( C \) and \( V_t \) are Jordan regions. The mapping \((\mathbf{u}, t) \to \phi_t(\mathbf{u})\) is assumed to be 1-1 and
continuously differentiable and $\phi_t(u) = x(u, t)$. A change of variable transforms the integral from one over a moving domain $V_t$ to one over a fixed domain $C$.

For a fixed $t$, the Jacobian matrix of $\phi_t$ is

$$\frac{\partial x}{\partial u} = \left[ \frac{\partial x^i}{\partial u^j} \right].$$

The Jacobian matrix of $\phi_t$ is nonsingular everywhere, and its inverse is $\frac{\partial u}{\partial x} = \left[ \frac{\partial u^i}{\partial x^j} \right]$. The Jacobian of $\phi_t$ is the determinant of the Jacobian matrix $\left| \frac{\partial x}{\partial u} \right|$. A formula from determinant theory is used, which says: if $A = A(t)$ is a nonsingular matrix function and $\det(A) \neq 0$, then

$$\frac{d}{dt} \left| \frac{\partial x}{\partial u} \right| = \left| \frac{\partial x}{\partial u} \right| \frac{d}{dt} \left( \det A \frac{\partial x}{\partial u} \right),$$

(4)

where $[\text{D det } A]$ is the directional derivative of $\det A$ in the direction $\dot{A}$. A proof of (4) is shown at the end. Apply formula (4) to the Jacobian matrix of $\phi_t$. First note that $\left( \frac{\partial x^i}{\partial u^j} \right) \cdot \dot{\frac{\partial u^i}{\partial u^j}} = \dot{\frac{\partial v^i}{\partial u^j}}$. So

$$\frac{d}{dt} \left| \frac{\partial x}{\partial u} \right| = \left| \frac{\partial x}{\partial u} \right| \text{tr} \left( \frac{\partial x}{\partial u} \right)^{-1} \left( \frac{\partial x}{\partial u} \right) = \left| \frac{\partial x}{\partial u} \right| \sum_{i,j} \frac{\partial v^i}{\partial u^j} \frac{\partial u^j}{\partial x^i} \frac{\partial x^i}{\partial u^j} = \left| \frac{\partial x}{\partial u} \right| \nabla \cdot \mathbf{v}.$$

The result is

$$\frac{d}{dt} \left| \frac{\partial x}{\partial u} \right| = \left| \frac{\partial x}{\partial u} \right| \nabla \cdot \mathbf{v}. \quad (5)$$

Let $f(t) = \iiint_{V_t} F(x, t) \, dx^1 dx^2 dx^3$. By a change of variables,

$$f(t) = \iiint_C F(x(u, t), t) \left| \frac{\partial x}{\partial u} \right| du^1 du^2 du^3.$$

The domain has changed from a moving domain $V_t$ to a fixed domain $C$. Now we can
use (3) to differentiate over the fixed domain \( C \) and then change back to \( V_t \).

\[
\frac{d}{dt} [f(t)] = \frac{d}{dt} \iiint_C F[x(u,t), t] \left| \frac{\partial x}{\partial u} \right| \, du \, du^2 \, du^3 \\
= \iiint_C \left[ \left( \sum_i \left( \frac{\partial F}{\partial x^i} \frac{\partial x^i}{\partial t} \right) \right) \left| \frac{\partial x}{\partial u} \right| + F[x(u,t), t] \left| \frac{\partial x}{\partial u} \right| \nabla \cdot \mathbf{v} \right] \, du \, du^2 \, du^3 \\
= \iiint_C \left[ \left( \sum_i \left( \frac{\partial F}{\partial x^i} \frac{\partial x^i}{\partial t} \right) + \frac{\partial F}{\partial t} \right) \left| \frac{\partial x}{\partial u} \right| + F[x(u,t), t] \left| \frac{\partial x}{\partial u} \right| \nabla \cdot \mathbf{v} \right] \, du \, du^2 \, du^3 \\
= \iiint_V \left( \nabla F \cdot \mathbf{v} + \frac{\partial F}{\partial t} + F \nabla \cdot \mathbf{v} \right) \, dx^1 \, dx^2 \, dx^3 \\
= \iiint_V \left( \nabla \cdot (F \mathbf{v}) + \frac{\partial F}{\partial t} \right) \, dx^1 \, dx^2 \, dx^3
\]

\[
\square
\]

Before proving formula (4) used in Leibniz’s rule, we first need to learn how to compute directional derivatives from the derivative.

**Proposition 1** If \( U \subset \mathbb{R}^n \) is open and \( f : U \to \mathbb{R}^m \) is differentiable at \( a \in U \), then all directional derivatives of \( f \) at \( a \) exist, and the directional derivative in the direction \( \mathbf{v} \) is given by

\[
\lim_{h \to 0} \frac{f(a + h\mathbf{v}) - f(a)}{h} = [Df(a)] \mathbf{v}.
\]

**Proof.** Define the “remainder” \( r(\mathbf{h}) \), a function of \( \mathbf{h} \), as

\[
r(\mathbf{h}) = \left( f(a + h\mathbf{v}) - f(a) \right) - [Df(a)] \mathbf{h}.
\]

The “remainder” is the difference between the increment to the function and its linear approximation. Since \( f \) is differentiable at \( a \),

\[
\lim_{\mathbf{h} \to 0} \frac{r(\mathbf{h})}{|\mathbf{h}|} = \mathbf{0}.
\]

Substituting \( h\mathbf{v} \) for \( \mathbf{h} \) equation (7), we find

\[
r(h\mathbf{v}) = \left( f(a + h\mathbf{v}) - f(a) \right) - [Df(a)] h\mathbf{v}.
\]

Dividing by \( h \) on both sides of the preceding equation gives

\[
|\mathbf{v}| \frac{r(h\mathbf{v})}{h|\mathbf{v}|} = \frac{f(a + h\mathbf{v}) - f(a)}{h} - [Df(a)] \mathbf{v}.
\]
Taking the limit as $h \to 0$ on both sides, the term $\frac{r(h\vec{v})}{h|\vec{v}|}$ goes to $\vec{0}$ by equation (6). So

$$\vec{0} = \lim_{h \to 0} \frac{f(a + h\vec{v}) - f(a)}{h} - [Df(a)] \vec{v}$$

(11)
or

$$[Df(a)] \vec{v} = \lim_{h \to 0} \frac{f(a + h\vec{v}) - f(a)}{h}. \tag{12}$$

\[\begin{align*}
\text{Theorem 2 (Derivative of the determinant)} \\
1. \text{The determinant function } & \det : \mathbb{R}^{n^2} \to \mathbb{R} \text{ is differentiable.} \\
2. \text{The derivative of the determinant at the identity is given by } & [D \det(I)] B = \text{tr}B. \\
3. \text{If } & \det A \neq 0, \text{ then } [D \det(A)] B = \det A \text{ tr}(A^{-1}B). \\
\end{align*}\]

\textbf{Proof.}

1. The determinant is a polynomial made up of the entries of the matrix, so the determinant is differentiable.

2. From the Proposition 1, we can compute the directional derivative

$$[D \det(I)] = \lim_{h \to 0} \frac{\det(I + hB) - \det I}{h}. \tag{13}$$

In evaluating the limit, the only terms that survive are the terms that are linear in $h$ of

$$\det(I + hB) = \det \begin{bmatrix}
1 + hb_{11} & hb_{12} & \cdots & hb_{1n} \\
hb_{21} & 1 + hb_{22} & \cdots & hb_{2n} \\
\vdots & \vdots & \ddots & \vdots \\
hb_{n1} & hb_{n2} & \cdots & 1 + hb_{nn}
\end{bmatrix} \tag{14}$$

To avoid fully computing the determinant, we examine the permutations of the entries. The only permutation that have terms linear in $h$ is the permutation involving the diagonal entries,

$$(1 + hb_{11})(1 + hb_{22}) \cdots (1 + hb_{nn}) = 1 + h(b_{11} + b_{22} + \cdots + b_{nn}) + \cdots + h^n b_{11} b_{22} \cdots b_{nn}. \tag{15}$$

Any permutation that involves an off diagonal entry will result in higher order terms since every off diagonal entry contains a factor of $h$. The linear term in (13) is

$$b_{11} + b_{22} + \cdots + b_{nn} = \text{tr}B. \tag{16}$$
3. Again, use Proposition 1 to take the directional derivative

\[ [D \det(A)] B = \lim_{h \to 0} \frac{\det(A + hB) - \det A}{h} = \lim_{h \to 0} \frac{\det(A(I + hA^{-1}B) - \det A}{h} \]

\[ = \lim_{h \to 0} \frac{\det A \det(I + hA^{-1}B) - \det A}{h} = \det A \lim_{h \to 0} \frac{\det(I + hA^{-1}B) - 1}{h} \]

\[ = \det A \lim_{h \to 0} \frac{\det(I + hA^{-1}B) - \det I}{h} = \det A \text{tr}(A^{-1}B) \quad (17) \]

In the case of Leibniz’s rule, \( B = \dot{A} \).