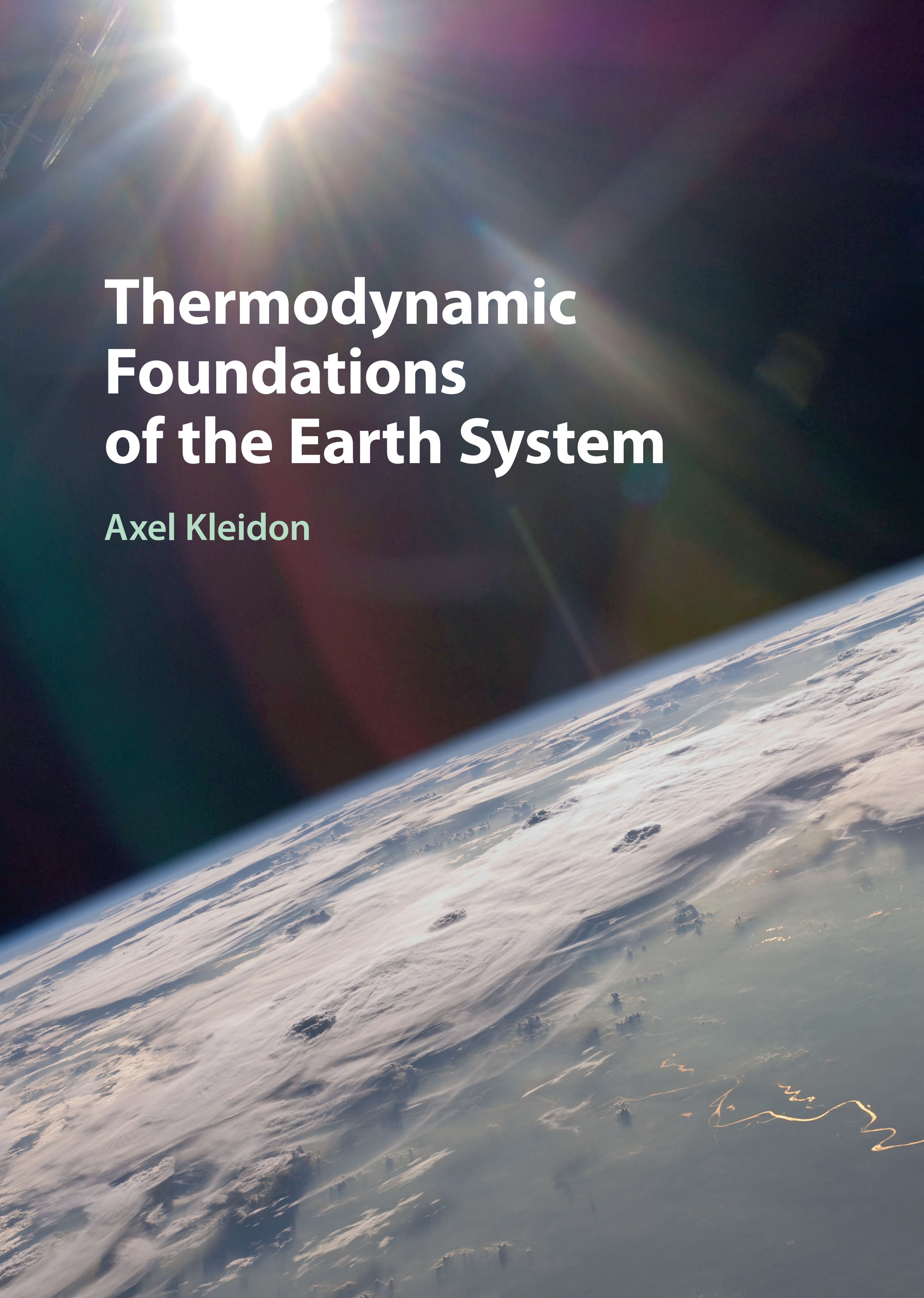

Thermodynamic Foundations of the Earth System

Axel Kleidon

THERMODYNAMIC FOUNDATIONS OF THE EARTH SYSTEM

Thermodynamics sets fundamental laws for all physical processes and is central to driving and maintaining planetary dynamics. But how do Earth system processes perform work, where do they derive energy from, and what are the ultimate limits?

This accessible book describes how the laws of thermodynamics apply to Earth system processes, from solar radiation to motion, geochemical cycling and biotic activity. It presents a novel view of the thermodynamic Earth system that explains how it functions and evolves, how different forms of disequilibrium are being maintained, and how evolutionary trends can be interpreted as thermodynamic trends. It also places human activity into a new perspective in which it is treated as a thermodynamic Earth system process.

This book uses simple conceptual models and basic mathematical treatments to illustrate the application of thermodynamics to Earth system processes, making it ideal for researchers and graduate students across a range of Earth and environmental science disciplines.

AXEL KLEIDON leads a research group in Biospheric Theory and Modelling at the Max-Planck-Institute for Biogeochemistry, Jena, Germany. He uses thermodynamics to quantify natural energy conversions within the Earth system and their limits, and applies this approach to understand atmosphere-biosphere interactions, Earth system responses to global change, and the natural limits of renewable energy.

THERMODYNAMIC FOUNDATIONS OF THE EARTH SYSTEM

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Preface

This book is about how thermodynamics applies to the Earth system. It is less about thermodynamics itself, but rather about how it applies to Earth system processes, their interactions, and the operation of the Earth system as a whole.

The motivation for writing this book stems from my interest in gaining a better, and more profound understanding of the Earth system, of the role that life plays within the system, and of how human activity changes the Earth system at a time when humans increasingly alter the operation of the planet. One way to deal with this challenge is to build increasingly comprehensive, yet also increasingly incomprehensible models of the Earth system. The other way is to search for a fundamental missing constraint that describes in comparably simple terms how systems operate and evolve. Since my doctoral work I have increasingly concentrated on this search. I looked into optimality approaches in vegetation, the Gaia hypothesis, and worked on the proposed principle of maximum entropy production (MEP). Over the years, I had many discussions with colleagues and took part in several workshops on these topics. I am tremendously thankful for these stimulating discussions, as these ultimately helped to shape my understanding that is now described in this book.

Today I think the answer to this missing constraint lies in the second law of thermodynamics. This law formulates a fundamental direction in physics that requires entropy to increase, at the small scale of an engine as well as at the scale of the whole Universe. Yet, its application to Earth system processes is almost absent, particularly when dealing with the whole Earth system. The second law, jointly with a thermodynamic formulation of the different processes yields a foundation to Earth system science that expresses processes in the same units of energy; it allows us to describe evolutionary dynamics as a thermodynamic direction imposed by the second law, and it sets fundamental limits and constraints on the emergent dynamics and interactions within the system. These limits can be quantified and yield estimates for Earth system processes that are largely consistent with observations, but require hardly any empirical parameters, substantiating that the second law provides missing constraints. It thus yields a grand picture of the Earth system in which its dynamics and evolution are a manifestation of the second law, a picture that is largely consistent with current descriptions yet yields a few critical insights that are not apparent from common formulations of the Earth system.

I think that these profound insights from thermodynamics should be accessible to a broad audience in the geosciences. Unfortunately, most books on non-equilibrium thermodynamics are only accessible to a highly specialized readership. Over the years I encountered several colleagues who studied thermodynamics yet still found it difficult to grasp, and this includes myself. Yet, I find this really unfortunate because thermodynamics can be fun and provides an elegant and simple way to look at the Earth system. For this view, it does not require much thermodynamic details to recognize its relevance and to use it for first-order estimates. In this book I aim to make thermodynamics accessible and thus describe only the bare essentials that are needed to formulate Earth system processes in thermodynamic terms.

To accomplish such an interdisciplinary, thermodynamic description of the whole Earth system, from radiation to human activity, poses a challenge as it requires a broad range of processes to be described. I therefore decided to focus on the mere minimum of thermodynamics and of Earth system processes to understand how thermodynamics applies to them and how these processes relate to each other. The book is thus not a comprehensive review of thermodynamics and its applications to Earth system processes. The text then includes references to related literature, and I apologize to those that I may have missed or that I may not have represented adequately. This led to a structure in which after the introduction, Chapters 2–5 provide the background in thermodynamics while the major processes of the Earth system are covered in Chapters 6–11. Chapter 12 closes with a synthesis to yield the perspective of the thermodynamic Earth system and how it can yield insights for Earth system science. Each chapter aims to be relatively self-contained and follows a similar format. It starts with a general introduction and closes by placing the material of the chapter back into the context of the Earth system and describes the linkages to the other chapters. By describing a broad range of processes across disciplines, one practical challenge was the mathematical formulation, as the letters of the alphabet are used for different variables in different disciplines. The letter G, for instance, is used for the gravitational constant, but also for Gibbs free energy. I tried to compromise and used mostly the convention of the different disciplines, so that some symbols refer to different aspects in different chapters. To help avoid confusion, the symbols are summarized in a table at the beginning of the book. Furthermore, a glossary includes brief explanations of the most central terms.

Even though the book was not written as a textbook, it is written at a level accessible to an audience in Earth and environmental sciences and is suitable for a course at the graduate level. As it involves the physical formulation of the different Earth system processes, the reader does require a certain level of familiarity with basic physics. The book illustrates the basic concepts associated with thermodynamics at a qualitative level supported by illustrations, and then uses comparatively simple models to demonstrate the application of thermodynamics and to estimate limits that predict magnitudes of different Earth system processes. These simple models are certainly not meant to be complete, but rather provided as an illustration of how thermodynamics is applied and how it can be used to establish magnitudes of Earth system processes.

This book would have been impossible to write without the substantial support and many stimulating discussions on various aspects of the Earth system as well as thermodynamics with colleagues and within my research group over the years. The number of colleagues are too many to list here, but I am very thankful for the stimulating discussions we had, for the disciplinary knowledge they provided, and for answering the seemingly strange questions that I sometimes asked. From my research group, I thank James Dyke, Fabian Gans, Lee Miller, Philipp Porada, Maik Renner, Stan Schymanski, Eugenio Simoncini, and Nathaniel Virgo for the many discussions we had on entropy, life, Earth, and the universe. I thank Uwe Ehret and Christian Reick for thoroughly reading through the draft of the book, providing constructive feedback, identifying unclear passages, and finding errors. I thank Cambridge University Press, particularly Susan Francis and Zoë Pruce, for their support and insistence to bringing this book to completion. Last, but not least, I thank my partner, Anke Hildebrandt, for her support at critical points and times in this and other projects. She and our kids were very patient, tolerated entropy discussions at the dinner table over the years, and accepted the time I spent in the last year to complete this book.

I hope you will find this book useful in providing a starting point to more applications of thermodynamics to Earth system science. I would be curious to hear back from the reader about any comments, suggestions, or activities to which this book may have helped to contribute.

Axel Kleidon

Symbols

Overview of the most frequently used symbols in the book, which may be supplemented by additional indices. For those symbols that are used to describe more than one property, the section or chapter where the respective symbol is being used is also given. Note that some variables, such as fluxes, are also used in reference to unit area.

Symbol	Description	Units	Value	Primary use
α	albedo	frac.	-	sec. 6.3.3
A	chemical affinity of a reaction	J mol^{-1}	-	sec. 9.2
A	area (typically surface area)	m^2		
B	geometric factor	-	-	
c	speed of light	m s^{-1}	$3 \cdot 10^8$	chap. 6
c	heat capacity	J K^{-1}		
c_p	specific heat capacity at constant pressure	J kg^{-1} K^{-1}	-	
c_v	specific heat capacity at constant volume	J kg^{-1} K^{-1}	-	
C	energy conversion rate (within Lorenz cycle)	W	-	sec. 7.3
C	condensation rate	kg m^{-2} s^{-1}	-	sec. 8.2
C_d	drag coefficient	-	-	sec. 7.3
d_e	mean distance of Earth to Sun	m	$150 \cdot 10^9$	
D	dissipation rate	W	-	
e	partial pressure of water vapor	Pa	-	
e_{sat}	partial pressure of water vapor at saturation	Pa	-	
E	evaporation rate	kg m^{-2} s^{-1}	-	
ϵ	dilution factor	-	-	chap. 6
ϵ_{lue}	light use efficiency	μmol CO$_2$ (μmol PAR)$^{-1}$	-	sec. 10.6
ϵ_{wue}	water use efficiency	g CO$_2$ (kg H$_2$O)$^{-1}$	-	sec. 10.6

Symbol	Description	Units	Value	Primary use
η	efficiency (= power/flux)	frac.	-	
f	fraction	frac.	-	
f	feedback factor	-	-	chap. 5
f	Coriolis parameter	$\mathrm{s^{-1}}$	-	sec. 7.6
f_w	water limitation factor	frac.	-	sec. 10.4
F	Helmholtz free energy	J	-	sec. 3.5
F	force	$\mathrm{kg\ m\ s^{-2}}$	-	sec. 4.6
ϕ	geopotential	$\mathrm{m^2\ s^{-2}}$		sec. 2.3.4
ϕ	latitude	°		chap. 7
g	gravitational acceleration	$\mathrm{m\ s^{-2}}$	9.81	
G	gravitational constant	$\mathrm{m^3\ kg^{-1}\ s^{-2}}$	$6.67 \cdot 10^{-11}$	sec. 2.3.4
G	generation rate (power)	W	-	
G	Gibbs free energy	J	-	sec. 3.5, chap. 9
ΔG_r	Gibbs free energy of a reaction	J	-	chap. 9
γ	psychrometric constant	$\mathrm{Pa\ K^{-1}}$	≈ 65	
Γ_d	dry adiabatic lapse rate	$\mathrm{K\ m^{-1}}$	$9.81 \cdot 10^{-3}$	
Γ_{dew}	lapse rate of the dew point	$\mathrm{K\ m^{-1}}$	$1.8 \cdot 10^{-3}$	
H	enthalpy	J	-	sec. 3.5
H	sensible heat flux	$\mathrm{W\ m^{-2}}$	-	chap. 10
h	Planck’s constant	J s	$6.63 \cdot 10^{-34}$	
I	current	A	-	
i	van’t Hoff factor	-	-	
J	heat flux	W	-	
J_{in}	influx of energy	W	-	
J_{out}	outflux of energy	W	-	
J_s	entropy flux	$\mathrm{W\ K^{-1}}$	-	chap. 2
J_m	mass flux	$\mathrm{kg\ s^{-1}}$	-	
J_{mom}	momentum flux	$\mathrm{kg\ m\ s^{-3}}$	-	
k	conductivity	$\mathrm{W\ K^{-1}}$	-	
k	friction coefficient	(depends)	-	sec. 4.6
k_b	Boltzmann’s constant	$\mathrm{J\ K^{-1}}$	$1.38 \cdot 10^{-23}$	
k_f	forward constant for chemical reactions	$\mathrm{mol\ l^{-1}\ s^{-1}}$	-	sec. 9.2
k_r	reverse rate constant for chemical reactions	$\mathrm{mol\ l^{-1}\ s^{-1}}$	-	sec. 9.2
k_r	radiative linearization constant	$\mathrm{W\ m^{-2}\ K^{-1}}$	-	
K_ν	spectral energy density	$\mathrm{J\ sr^{-1}\ m^{-2}}$	-	sec. 6.2
K_{eq}	equilibrium constant	-	-	sec. 9.2
L	length	m	-	
L_ν	spectral entropy density	$\mathrm{J\ sr^{-1}\ m^{-2}\ K^{-1}}$	-	sec. 6.2
λ	wavelength	m	-	chap. 6
λ	latent heat of vaporization	$\mathrm{J\ kg^{-1}}$	$2.5 \cdot 10^{6}$	chap. 8, chap. 10
λE	latent heat flux	$\mathrm{W\ m^{-2}}$	-	

Symbol	Description	Units	Value	Primary use
μ	chemical potential	J mol^{-1}		
m	mass	kg	-	
n	molar mass	kg mol^{-1}	-	
N	number of particles	- or mol	-	sec. 2.4.1
N_ν	distribution function	-	-	sec. 6.2
N	Nusselt number	-	-	sec. 7.7
ν	frequency	s^{-1}	-	
Ω	solid angle	sr	-	chap. 6
Ω_{sun}	solid angle of the Sun in the Earth’s sky	sr	$6.8 \cdot 10^{-5}$	chap. 6
Ω	Earth’s angular velocity	s^{-1}	$7.27 \cdot 10^{-5}$	sec. 7.6
p	pressure	Pa	-	
p_s	surface pressure	Pa	$1.01325 \cdot 10^5$	
p	radiation pressure	Pa	-	sec. 6.2
p	probability	-	-	sec. 3.3
π	osmotic pressure	Pa	-	
q	specific humidity	kg kg^{-1}	-	
Q	amount of heat added or removed	J	-	
Q	charge	C	-	sec. 4.6
Q	runoff	kg m^{-2} s^{-1}	-	sec. 10.4
ρ	density	kg m^{-3}	-	
r_{sun}	radius of the Sun	m	$695.8 \cdot 10^6$	
r_e	radius of the Earth	m	$6.372 \cdot 10^6$	
R	ideal gas constant	J kg^{-1} K^{-1}	287 (air)	
		J kg^{-1} K^{-1}	461 (water vapor)	
		J mol^{-1} K^{-1}	8.314 (general)	
R_{in}, R_{out}	radiative flux	W m^{-2}	-	
R_l	flux of terrestrial radiation	W m^{-2}	-	
$R_{l,\text{up}}$	flux of terrestrial radiation (upwards) at the surface	W m^{-2}	-	
$R_{l,\text{down}}$	flux of terrestrial radiation (downwards) at the surface	W m^{-2}	-	
$R_{l,\text{net}}$	net flux of terrestrial radiation at the surface	W m^{-2}	-	
$R_{\text{sun,tot}}$	solar luminosity	W	$7.6 \cdot 10^{26}$	
$R_{s,\text{in}}$	influx of solar radiation at the top of the atmosphere	W m^{-2}	1370	
R_s	flux of solar radiation	W m^{-2}	-	
$R_{s,a}$	absorbed solar radiation in the atmosphere	W m^{-2}	≈ 75	
$R_{s,s}$	absorbed solar radiation at the surface	W m^{-2}	≈ 165	
$R_{s,\text{toa}}$	total absorbed solar radiation	W m^{-2}	≈ 240	
R	resistance	Ω	-	sec. 4.6

Symbol	Description	Units	Value	Primary use
s	slope of the saturation vapor pressure curve, $s = de_{\text{sat}}/dT$	Pa K^{-1}	-	
S	thermal entropy	J K^{-1}		sec. 2.3.2
S	radiation entropy	J K^{-1}	-	sec. 6.2
σ	Stefan-Boltzmann constant	W m^{-2} K^{-4}	$5.67 \cdot 10^{-8}$	sec. 6.2
σ	entropy production	W K^{-1}	-	
t	time	s	-	
Δt	time interval	s	-	
T	temperature	K	-	
T_a	atmospheric temperature	K	-	
T_e	engine temperature	K	-	
T_r	radiative temperature	K	≈ 255	
T_s	surface temperature	K	-	
T_{sun}	emission temperature of the Sun	K	5760	
θ	potential temperature	K	-	
τ	residence time or time scale	s	-	chap. 2, chap. 5
τ	optical depth	-	-	chap. 6
u	energy density	J m^{-3}	-	chap. 6
u	velocity (zonal component)	m s^{-1}	-	chap. 7
U	internal energy	J	-	
U_{rad}	radiative energy	J	-	
U_{te}	thermal energy	J	-	
U_{pV}	uncompensated heat	J	-	
U_{pe}	potential energy	J	-	
U_{ke}	kinetic energy	J	-	
U_{be}	binding energy	J	-	
U_{other}	other, non-thermal form of energy	J	-	
U	voltage	V	-	sec. 4.6
U	heat storage	J m^{-2}	-	sec. 10.3
v	velocity (general, or meridional component)	m s^{-1}	-	chap. 7
v	reaction velocity	mol s^{-1} l^{-1}	-	sec. 9.2
V	volume	m^3	-	
W	number of possible arrangements	-	-	sec. 2.4.1
W	work	J	-	
W_s	soil water content	kg m^{-2}	-	sec. 10.4
x	horizontal dimension	m	-	
ξ	extent of reaction	mol	-	
X	dilution effect on entropy	-	-	sec. 6.3
y	horizontal dimension	m	-	
Δz	vertical thickness	m	-	
z	vertical coordinate	m	-	
z_0	scaling height in the barometric formula	m	≈ 8425	

1

Thermodynamics and the Earth system

1.1 A thermodynamic basis for Earth system science

The Earth is a vastly complex system. This complexity is reflected in the broad range of processes that it entails, from the solar radiative forcing to the highly dynamic circulatory patterns in the atmosphere, ocean and the interior, to high level and diversity of metabolic activity of life, and to human activities. The complexity is further enhanced by strong interactions by which processes alter their own drivers. Atmospheric motion, for instance, transports such vast amounts of heat that it alters the radiative exchange with space. The activity of the Earth’s biosphere, the sum of all living organisms, has strongly altered the chemical composition of the atmosphere, as for instance reflected in its high abundance of molecular oxygen, resulting in altered physical and chemical conditions. And finally, human activity over the last century has released such large amounts of buried organic carbon by its industrial activities that it has substantially altered the global carbon cycle resulting in enhanced concentrations of carbon dioxide in the atmosphere and global climate change. With such complexities in mind, it would seem almost impossible to make robust predictions of magnitudes, the strength of interactions, and the overall evolutionary direction of the Earth system as a whole in order to get a robust, physical understanding of how the whole Earth system functions and responds to change.

Yet there is a range of fundamental, practical, and relevant questions that require such a robust understanding. What determines, for instance, the strength of the atmospheric circulation and its ability to transport and mix heat and mass? The answer to this question would help us to make better predictions of the magnitude of climate system processes and how these would respond to perturbations and change. Does the climate system, and the planet as a whole, regulate its climatic state to some particular reference level? Is climate even regulated to a point that is most suitable to life, because of the presence of life, as proposed by the Gaia hypothesis (Lovelock 1972b,a; Lovelock and Margulis 1974)? If this is so, how would human activity play into such a planetary regulation? A better understanding of these questions would provide information about the role of the biosphere at the planetary scale and the factors that shape planetary habitability. What are the limits to human activity, for instance, limits related to food production and the availability of renewable energy and how do these relate to the functioning of the planet? What are the associated human impacts on the system, and can these impacts tip the planet off some edge into an inhabitable state? The answer to this question would help us to develop better scenarios of a sustainable future. What these questions have in common is that they require a perspective on the whole Earth system, as the limits that these questions involve are of a physical nature, and ultimately relate to the planetary forcing represented by solar radiation and the cooling of the interior Earth.

The goal of this book is to provide a fundamental basis rooted in physics that allows to approach these questions. This book will show that a central component for this basis is described by thermodynamics, a fundamental theory in physics that deals with conversions of energy and their direction towards states of higher entropy. It is particularly the latter aspect, known as the second law of thermodynamics, that has intrigued many scientists, that provides a fundamental direction for processes, and that sets fundamental limits. Energy and entropy are very basic quantities that apply to practically all processes, from radiation to metabolic and human activity. Thermodynamics thus provides a way to formulate all Earth system processes in comparable quantities, thus providing a general accounting basis.

Yet, it is not just the thermodynamic formulation that is important. Equally important is to place the thermodynamic formulation into a systems perspective of the whole Earth system. This combination allows us to link processes to their ultimate driver of solar radiation and interior heat through sequences of conversions. These conversions are associated with converting energy of different forms, and the laws of thermodynamics constrain these conversions by thermodynamic limits. When thermodynamic limits are then applied to these sequences, we can quantify the limits on their rates and on the interactions that result from these processes. As we will see in the book, these limits provide basic and robust estimates for a range of Earth system processes that compare well with observations. This is not because these processes are organized in a simple, predictable way, but rather likely because they are so complex and have evolved so far that they operate near their thermodynamic limit. Even if not all processes may necessarily operate near their limit, it nevertheless provides us with an evolutionary "target" that can be used to interpret evolutionary dynamics, and it can be used to yield relatively simple and transparent estimates for the magnitude of processes that typically require only a mere minimum of empirical knowledge. This view may then already provide sufficient information to understand Earth system processes, how they respond to change, how life and human activity fit in and what a sustainable future may look like.

In the remaining part of this chapter, the basics of thermodynamics are described qualitatively, with the details being described in Chapter 3. It is illustrated how systems are maintained in an ordered state by fluxes of different entropy going through the system, and how this relates to living organisms and the Earth system as a whole. It is then explained how these basic components of thermodynamics result in limits to the ability to perform work, and how this work feeds sequences of energy conversions of different processes. At the end of this chapter, an overall view of the thermodynamic Earth system is given and it is described how this view is partitioned into the different chapters of the book.

1.2 Thermodynamics in a nutshell

Thermodynamics sets the rules for the conversions of energy from one form into another and sets the general direction into which these conversions take place. These two aspects are described by the first and second law of thermodynamics. The first law essentially states the conservation of energy. When energy is converted from one form into another, overall no energy is lost or gained. As energy is converted, its concentration, or reversely, its dispersal is altered. The extent of energy dispersal during a conversion is described by entropy, with more dispersed forms of energy corresponding to a higher entropy. The second law states that energy is, overall, increasingly being dispersed. This dispersal of energy is, for instance, reflected when a heated object such as a hot cup of coffee cools down and approaches the temperature of its surroundings. Here, the first law would tell us that the heat given off by the object is added to the heat content of the surroundings so that the total energy of the object and its surroundings is conserved. The dispersal of heat that is associated with the cooling of the object, however, is not captured by the first law. This tendency is rather the manifestation of a profound direction of nature to spread energy, mass, and other physical attributes into uniform concentrations. Such states of uniformity are described in thermodynamics as states of maximum entropy, or thermodynamic equilibrium. The natural direction of processes to spread energy and to increase entropy is described by the second law of thermodynamics.

These two laws of thermodynamics, the conservation of energy, and the increase in entropy, are so general, that Albert Einstein once said that (Klein 1967):

> "[a] theory is more impressive the greater the simplicity of its premises, the more different are the kinds of things it relates, and the more extended its range of applicability. Therefore, the deep impression which classical thermodynamics made on me. It is the only physical

theory of universal content, which I am convinced, that within the framework of applicability of its basic concepts will never be overthrown."

The second law in particular sets such a profound direction for physical processes that it has been labeled the "arrow of time" (Eddington 1928). The increase in entropy tells us something quite specific about how we would expect the dynamics within systems to take shape. No matter how complicated a system is, how large it is, or how many types of processes and constituents it involves, the overall dynamics that take place within the system must obey the laws of thermodynamics. Overall, energy needs to be conserved, and entropy needs to increase. How this increase in entropy is accomplished within a system is non-trivial as it also needs to consider how exchange fluxes across the system alter the entropy of the system.

One important characteristic of Earth system processes is that they typically operate far from thermodynamic equilibrium as gradients and fluxes are maintained within the system. This disequilibrium can be maintained in a steady state, in which the mean properties of the system do not change in time, without violating the laws of thermodynamics. The actual formulation of these laws is somewhat different and needs to account for the exchanges between the system and its surroundings across the system boundaries. These exchanges do not only exchange energy, mass, or other physical quantities, they also exchange entropy. When energy is added to warm places, and the same amount of energy is removed from cold places, the total energy within the system does not change, but a gradient in temperature is being maintained, reflecting disequilibrium. As this energy was added and removed at different temperatures, the exchange of entropy does not cancel out, but results in a net export of the entropy that is produced within the system so that the system can be maintained in a state of thermodynamic disequilibrium. In the application of the second law, this exchange of entropy needs to be taken into account. This exchange with the surroundings has important consequences for the state of a system: It allows a system to maintain a state away from thermodynamic equilibrium, and the entropy exchanges across the boundary reflects important information on the extent to which a system is maintained in a state of thermodynamic disequilibrium.

To illustrate this critical point in more detail, let us consider the two systems shown in Fig. 1.1. The top row of this figure shows a "system A" in which no exchange with its surroundings takes place. In such a setting, an initial internal difference in temperature would fade in time. Expressed differently, the processes within the system are directed to deplete this temperature difference. The total energy of the system during this redistribution of heat remains unchanged, but its distribution has changed. This latter aspect reflects the increase of entropy within the system. In the final state of a uniform temperature distribution, energy is distributed most uniformly within the system, the entropy is at a maximum, and this state corresponds to a state of thermodynamic equilibrium. This situation is akin

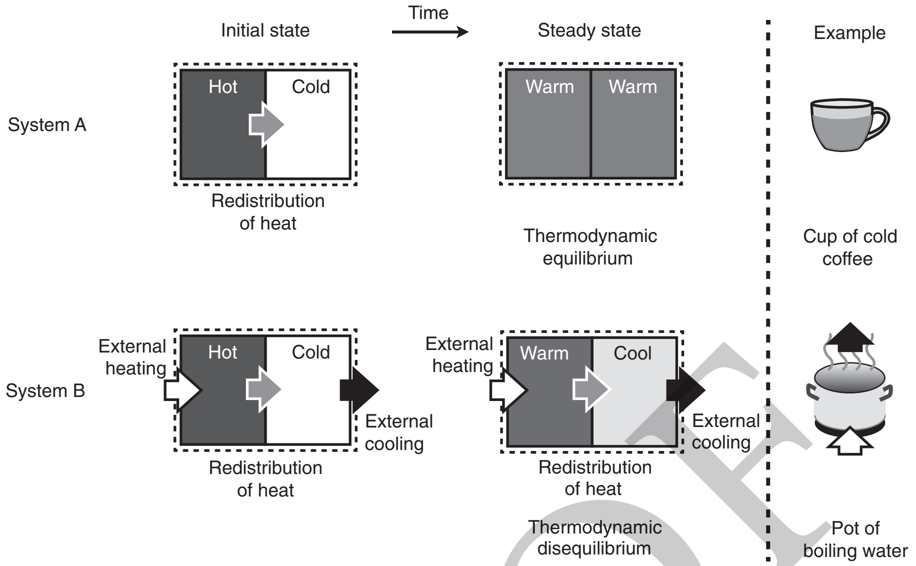

Figure 1.1 Two different types of systems (A: an “isolated” system; B: a “non-isolated” system) develop from an initial state to a final, steady state. An everyday example for such systems are given on the right.

to a hot cup of coffee in a room that would cool down to the temperature of the surroundings.

The bottom of Fig. 1.1 shows a “system B” in which heat is added to one side of the system, while it is cooled at the other side of the system. This setting is comparable to a pot of water on a stovetop that is heated from below, and cooled from above. Just as in the situation described earlier, the processes within the system are directed to deplete the temperature difference within the system, attempting to spread the heat uniformly within the system. However, since energy is continuously added and removed at different parts of the system boundary, the system is maintained in a state of disequilibrium. This disequilibrium manifests itself in the temperature difference that is being maintained within the system and that we can observe, but is also reflected in the dynamics that take place in the system. In the case of the pot of water, these dynamics are simply the convecting motion of boiling water within the pot.

To sum up, the two systems shown in Fig. 1.1 may look the same in terms of the amounts of heat that they contain, but they differ significantly in terms of the internal dynamics and their thermodynamic state. System A describes a system in which the final, steady state is a static state of thermodynamic equilibrium. The properties of the system do not change in time, there is no exchange in energy or entropy, and the system does not show any dynamics. System B also reaches a steady state in which the properties of the system do not change in time. However, its steady state is characterized by disequilibrium and reflects dynamics associated with the heat flux within the system. These dynamics are maintained by exchange fluxes, and the trend to deplete the temperature gradient within the system is mirrored by the entropy exchange of the system with its surroundings. This latter aspect, that the dynamics within the system are directed to deplete gradients, is not a consequence of energy conservation, but of the second law of thermodynamics. This steady state in which fluxes and gradients are being maintained in system B reflect thermodynamic disequilibrium and this state is being maintained by the entropy exchange of the system with its surroundings.

These considerations apply to the Earth system as well. As the Earth is a thermodynamic system that is maintained in a state with fluxes and gradients like system B, this thermodynamic view suggests that the dynamics that we can observe within the Earth system result as a consequence of the second law as well. A necessary foundation to implement these considerations is the formulation of the dynamics entirely in terms of energy and entropy exchange. This is not just captured by the Earth's energy balance, which is the common starting point in climatology. It also requires that all other processes are described in energetic terms, ranging from atmospheric motion to geochemical cycling, biotic and human activity. Furthermore, it requires a description of the entropy fluxes that are associated with these dynamics, which are rarely considered in Earth system science, yet central if we want to interpret the dynamics of the Earth system in terms of the second law.

1.3 Disequilibrium, life, and Earth

Entropy considerations are central when we want to understand how disequilibrium is being maintained and how highly complex phenomena such as life or the Earth system as a whole do not violate the second law, at each and every process and at the scale of the whole planet. In his seminal book on "What is life," Erwin Schrödinger (1944) described that a living organism satisfies the second law by consuming low-entropy food and producing high-entropy waste (Fig. 1.2a). Averaged over some time period, the food uptake by the organism roughly balances its waste, so that there is no net gain or loss of mass. The mass flux in itself does not contain the relevant information that would tell us that the organism is alive. That the influx of mass balances the outflux of mass is simply a consequence of the overall conservation of mass. The relevant information comes from the fact that the influx of mass is of a different constitution than the outflux. It is this difference in constitution that is captured by entropy, and it is this difference in entropy in the exchange of the living organism with its environment that allows the living organism to extract energy to run its metabolism. This metabolic energy is then dissipated and released as heat.

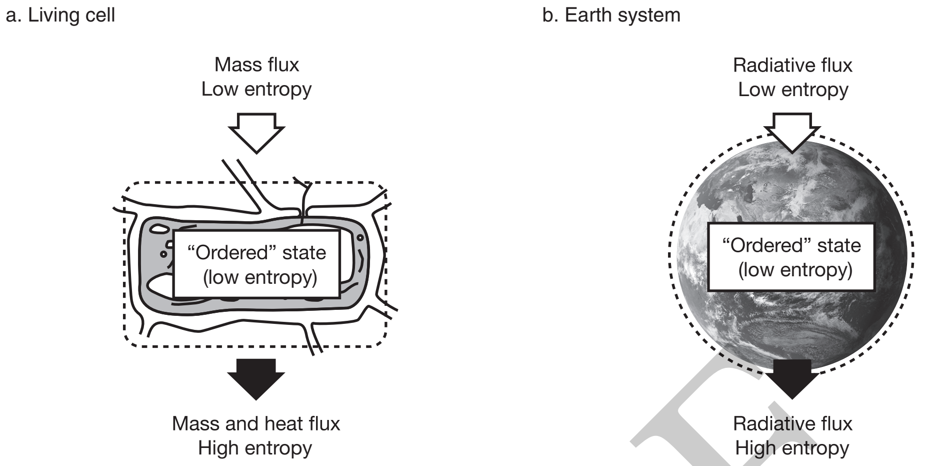

Figure 1.2 (a) A living cell and (b) the whole Earth system as examples of dissipative systems that are maintained far from thermodynamic equilibrium by the exchange of entropy. Source of Earth image: NASA.

A living organism is just one example of a so-called dissipative structure, a term introduced by Ilja Prigogine, a chemist who extensively worked on non-equilibrium thermodynamics and structure formation. His many accomplishments include textbooks on non-equilibrium thermodynamics (Prigogine 1962; Kondepudi and Prigogine 1998), and his major contributions are summarized in an article published on the occasion of the Nobel prize in Prigogine (1978). There are many more examples for such dissipative structures, ranging from the patterns that form in chemical reactions, convection cells in fluids, living organisms, and, ultimately, the whole Earth system. These structures have in common that they maintain states far away from thermodynamic equilibrium, and that these states are being maintained by the entropy exchange with the surroundings, just like the simple system B that was depicted in Fig. 1.1.

In the Earth system (Fig. 1.2b), the entropy exchange of all dissipative structures is ultimately integrated at the planetary scale to the entropy exchange with space. Just like a living organism is maintained by the entropy exchange associated with the fluxes of "food" and "waste," so is the activity of the whole Earth system being maintained by entropy exchange. The similarity between a living cell and the whole Earth as being dissipative structures was noted by James Lovelock and Lynn Margulis. It was this thermodynamic consideration that led Lovelock and Margulis to view the Earth system as a "superorganism" and to formulate the controversial Gaia hypothesis that compared the functioning of the Earth system to a living organism (Lovelock and Margulis 1974).

For the Earth system, the vast majority of entropy exchange is accomplished by the radiative exchange with space (Fig. 1.2b). The "food" of the Earth system is solar radiation, which has a low entropy because the radiative energy is composed of relatively short wavelengths, an aspect we get back to in Chapter 6. The "waste" of the Earth system is exported by the radiation emitted to space, which is radiation of relatively long wavelength and thus has a high entropy. As in the case of the living cell, we deal with a system in which the planetary energy balance is balanced, so that the total radiative energy absorbed by the Earth system roughly balances the total radiative energy emitted to space. The relevant difference is not contained in the energy fluxes, but rather in the associated fluxes of planetary entropy exchange. It is this planetary entropy exchange that allows the maintenance of thermodynamic disequilibrium as well as all the dissipative structures and activities that take place on Earth. Such a system with dissipative structures and net entropy exchange we refer to as a dissipative system, and to the processes that take place within the system and cause an increase in entropy as dissipative activity.

While living organisms and the Earth system both constitute dissipative systems, they do not act independently. In a system's view, the dissipative structures of living organisms feed on the boundary conditions set by the Earth system, yet the products of living organisms will affect their surroundings, and thereby alter the planetary system. This connection between life and the Earth system was formulated very nicely by Ludwig Boltzmann (1844–1906), a physicist who set much of the statistical foundation of thermodynamics. He expressed this connection as (Boltzmann 1886):

> "The general struggle for existence of living organisms is therefore not a struggle for the basic materials – these materials are abundantly available for organisms in air, water and soil – nor for energy, which is abundant in form of heat in any body, albeit unfortunately unavailable, but a struggle for entropy, which through the transformations of energy from the hot sun to the cold Earth becomes available. To fully explore this transformation, plants spread their leaves in unimaginable extent and force the solar energy to perform chemical synthesis in yet unexplored ways before this energy sinks to the temperatures of the Earth's surface. The products of this chemical kitchen forms the object of struggle for the animate world."

Note that Boltzmann formulated this relationship before much of the details involved in photosynthesis were discovered. This description of living organisms places biotic activity into a planetary context. Yet, before we describe these interdependencies and their implications in greater detail, we first explore what else thermodynamics can tell us about dynamics, interactions, and evolution.

1.4 Thermodynamic limits

So far, we described the first and second law of thermodynamics and how these provide a constraint and a direction for Earth system processes. When these two

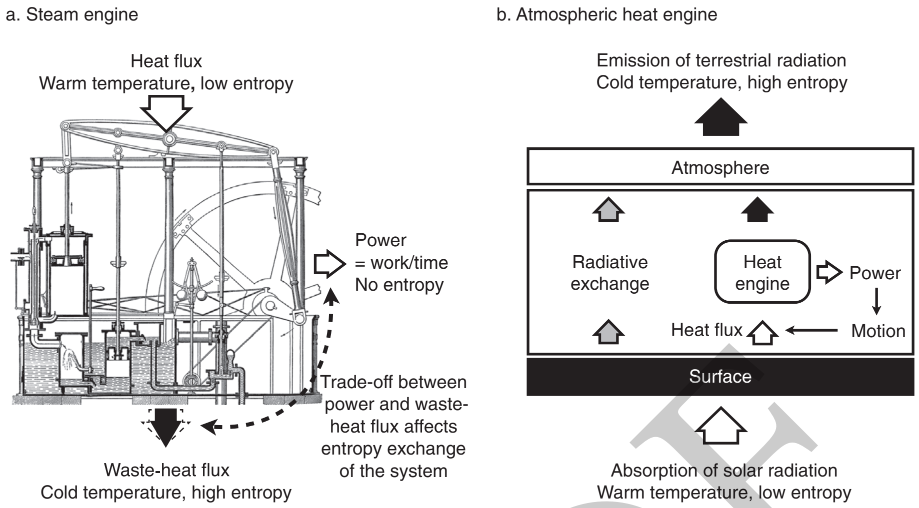

Figure 1.3 (a) Illustration of a heat engine using Watt's original steam engine as a template. Only a fraction of the heat flux into the engine can be converted to mechanical power because of the condition imposed by the second law. (b) An illustration of the surface-atmosphere system in which a heat engine generates motion from radiative heating of the surface and the cooling of the atmosphere. Steam engine image from Meyer (1886), available on www.wikipedia.org.

laws are being combined, they yield a fundamental limit on how much work can be performed, or, more generally, how much energy can be converted from one form into another. This limit constrains, for instance, how much of the radiative heating of the Earth's surface can be converted into the kinetic energy associated with atmospheric motion. The two laws thus set firm constraints on the magnitude of the dynamics that can take place within the Earth system as a result of the planetary forcing.

The limit for converting heat into mechanical work is known as the Carnot limit, named after the engineer Sadi Carnot (1796–1832), who was one of the pioneers in developing thermodynamics at the times at which steam engines were invented. The limit is illustrated in the following using the steam engine shown in Fig. 1.3a. This steam engine operates by the addition of heat at a high temperature, typically by the combustion of a fuel. This is shown in the figure by the white arrow at the top. The first law states that this addition of heat is balanced by the removal of "waste" heat through its exhaust at a colder temperature, shown by the black arrow at the bottom, and by the mechanical work (the white arrow on the right). The second law requires that the engine cannot decrease the overall entropy, but that it at best remains unchanged. This leads to a constraint on the entropy exchange of the engine, which is accomplished by the heat exchange at different temperatures.

The waste-heat flux plays a critical role, as it exports heat at a colder temperature and exports higher entropy to the surroundings of the engine. When the engine performs work, this must come at the expense of a reduced waste-heat flux. This follows from the first law. With a reduced waste-heat flux, less entropy is being exported, so that the net entropy exchange of the engine decreases the more work is being performed by the engine. The Carnot limit marks the point at which there is no net entropy exchange by the system, which is the absolute limit that is permitted by the second law. The work performed by the system then results in the generation of motion, that is, kinetic energy, or the lifting of mass against gravity, that is, potential energy. Hence, the Carnot limit describes the limit to energy conversions from heat to another form.

As already imagined by Carnot, this limit does not just apply to steam engines, but to "natural" engines that drive Earth system processes. In his book "Reflections on the motive power of fire" (Carnot 1824), he writes that:

> "The vast movements which take place on the Earth are ... due to heat. It causes the agitations of the atmosphere, the ascension of clouds, the fall of rain and of meteors, the currents of water which channel the surface of the globe, and of which man has thus far employed but a small portion. Even earthquakes and volcanic eruptions are the result of heat."

Carnot's writing suggests already back in the early nineteenth century that one should view these Earth system processes as if these operate like steam engines, or, more generally, heat engines, hypothetical devices that convert thermal energy into physical work. These engines would be subjected to the same Carnot limit as a heat engine in how much work these could perform and thus result in the dynamics that we can observe.

When formulating thermodynamic limits for Earth system processes, there are a few critical differences to the setup of a Carnot heat engine that need to be considered. An example of this application to atmospheric convection is shown in Fig. 1.3b. Firstly, the generation of atmospheric motion can be viewed as the result of an atmospheric heat engine that is constrained by the heating and cooling associated with radiative exchange. The setup of the Carnot limit does not, however, account for the fluxes of energy that bypass the engine. This aspect becomes important for the atmosphere, where radiation transports energy from the heated surface to the cold atmosphere and which cannot be utilized by the convective heat engine of the atmosphere. This bypass results in unavoidable entropy production within the system which can only be reduced, but not avoided. Secondly, the mechanical work that is derived from the engine actually feeds back upon itself. Atmospheric motion, for instance, results from this work being performed, yet atmospheric motion is associated with the heat flux that drives the engine. In other words, there are internal dynamics that take place within the system that we need to consider in the steady state that describe the strength of that engine. Thirdly, when the engine performs work and transports large amounts of heat, its driving temperature gradient does not remain unchanged, but is reduced. This effect is well known. The Earth's surface, for instance, is cooled rather substantially by the presence of convective heat fluxes, which implies that the vertical temperature difference is depleted by the convective flux. These effects have implications for the Carnot limit as they alter the entropy exchanges of the engine. As will be shown in Chapter 4, when these effects are being considered, the resulting limit to work is much lower than what would be expected from a naive application of the Carnot limit to Earth system processes.

1.5 Thermodynamics, evolutionary dynamics, and structures

Thermodynamic limits set a rigid, physical bound on Earth system processes, yet they say nothing about whether, why, and how a system would operate at this limit. This, then, becomes a question about what thermodynamics can tell us about a general, evolutionary direction of systems and how systems would need to be organized such that they reach their limits. This is quite a profound question. If the evolution of systems is such that the processes within evolve towards their thermodynamic limit, the final, steady state of the system becomes predictable simply by considering the thermodynamic limit. Then, the emergent dynamics may be extremely complex in detail, but the overall behavior of the system becomes simple as it is dominated by the overall constraint imposed by the thermodynamics of the system. This constraint specifically concerns the conditions at the system boundary as well as the entropy exchange of the system. The complexity reflected in the "details" within the system should still show some form of regularity, for instance in form of characteristic structures such as networks (Fig. 1.4), turbulent, or wave-like patterns. We can thus formulate a hypothesis that thermodynamic systems evolve towards their limit by the formation of structures, a hypothesis that we refer to here as "maximization by structures." This hypothesis intimately links the presence of such structures to differences in the dissipative behavior of the system, and links these to a general evolutionary direction of thermodynamic systems.

This question about the link among thermodynamics, evolution, and structures has long been explored. Several hypotheses or principles have been proposed, and some of these may sound contradictory to each other, but this contradiction can be resolved upon a closer look. Perhaps the first to formulate such a principle was Alfred Lotka (1880–1949), an engineer mostly known for his contribution to population biology. In two papers published in 1922 (Lotka 1922a,b), Lotka extended Boltzmann's notion of the "struggle for existence of living organisms" and argued that for biological evolution, "… natural selection tends to make the

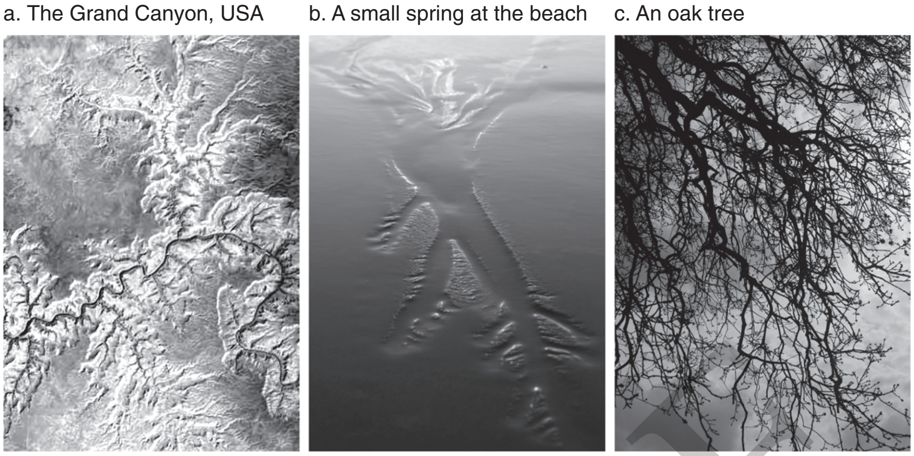

Figure 1.4 Examples of structures that illustrate non-uniform distribution of gradients and flows: (a) a section of the Grand Canyon; (b) a spring at a Danish beach; (c) branches of an oak tree. Sources: (a) terraprints.com/NASA; (b) and (c) the author.

energy flux through the system a maximum so far as compatible with the constraints to which the system is subject.” Hence, evolution should tend to make this energy flux a maximum. He noted that this energy flux relates to the power of the process, the physical work performed through time, and that this formulation of evolution and natural selection should make this power a maximum. Lotka focused in his description on the biosphere and its evolution, yet a similar, more general argument could be made for other, physical processes as well (Odum and Pinkerton 1955). This formulation of the maximum power principle combines a physical limit of maximum power with a general evolutionary trend towards this maximum.

There are a series of related thermodynamic extremum principles that have been proposed. There is, for instance, the statement that systems close to thermodynamic equilibrium minimize their entropy production (“MinEP”) that was formulated by Prigogine, and which has also been used in engineering (e.g., Bejan 1996). Seemingly contrary to this, a principle of maximum entropy production (“MEP”) has been formulated, originally in atmospheric sciences by the works of Paltridge (1975, 1978). This proposed principle of MEP has been shown to be rather successful in predicting the poleward heat transport and turbulent phenomena (e.g., Ozawa et al. 2003; Kleidon et al. 2010). On the other hand, the minimization of frictional dissipation or energy expenditure has been rather successful in explaining the fractal nature of vascular networks in biological systems (West et al. 1997) and river networks (Rinaldo et al. 1992; Rodriguez-Iturbe and Rinaldo 1997), such as those shown in Fig. 1.4. Minimization or maximization sounds rather contradictory, but when evaluating these propositions in more detail, these simply represent alternative views on the same system. If there are two different kinds of processes in a system, for instance radiative and convective heat transfer, but the boundary conditions of the system are fixed, then the maximization of the entropy production associated with one process inevitably results in the minimization of the other process. Likewise, the MEP hypothesis is closely related to Lotka's maximum power principle. As the performance of work results, in the end, in some form of dissipative heating as any motion is associated with frictional losses, it also results in entropy production. When such a system is viewed in a steady state in which its power is balanced by dissipation, the maximization of power is equivalent to the maximization of dissipation, which in turn is almost the same as the maximization of entropy production. This link among different thermodynamic optimality principles is described in Chapter 4 in greater detail.

While formulating a target, these extremum principles still say nothing about why and how systems should evolve to these states. A partial answer to this question was already formulated by Prigogine, who coined the expression of "order through fluctuations" (e.g., Prigogine et al. 1972). Even though Prigogine stated that there is no general thermodynamic extremum principle that describes systems far from equilibrium (e.g., Kondepudi and Prigogine 1998), he described a thermodynamically based, evolutionary feedback by which a thermodynamic system would increase its entropy production. Once a system surpasses a threshold, this would generate instabilities by fluctuations in the system, which in turn would cause greater entropy production by the system. A greater entropy production is maintained by greater entropy export and this would allow for the maintenance of a more ordered state, hence expressing these dynamics by the phrase "order through fluctuations." Such thresholds are found in many Earth system processes, from the threshold that characterizes the transition to turbulent flow, the threshold associated with the detachment of sediment in river systems, or the threshold of a minimum population size in ecology. We could thus envision that this basic thermodynamic mechanism of Prigogine applies to a whole range of Earth system processes up to the planetary scale and that would form a positive, dynamical feedback that enhances the growth of dissipative structures within the Earth system.

Yet, what is missing is a dynamic feedback that limits this growth so that a steady state is reached within the system. This is where thermodynamic limits come into play. They set a physical boundary to the dissipative behavior of a system through the entropy exchange with the surroundings. As dissipative structures grow and make up an increasing share of the entropy production within the system, they ultimately deplete the driving gradient that feeds their growth. This forms a relatively slow-acting negative feedback that should set limits to the growth of dissipative structures in their natural environment.

We can thus envision a general template of a sequence of dynamics that take place towards the thermodynamic limit, similar to those described in Kleidon et al.

(2013) for the thermodynamic evolution of river networks. This sequence starts with the system being in a state close to or at thermodynamic equilibrium. In case of water flow over a land surface, this initial state would be represented by a surface with a relatively uniform slope with no network that channels runoff to an outlet. When this system is perturbed, a small perturbation or fluctuation can cause the initiation of dynamics that further feeds its growth. For instance, a rainfall event may supply sufficient water flow that starts to detach sediment, starting the process of forming a channel. The removal of sediment at one site then locally steepens the gradient, which allows for more detachment at this site in relation to other parts of the slope. By developing such heterogeneous structures as in the case of river networks, the system can then channel its flows and reduce frictional losses within the structure, thereby further feeding the growth of structures and its dissipation. At one point, the structures would enhance fluxes to an extent such that the driving gradients are being depleted. Finally this last aspect is advanced to a point that further growth is counteracted by the depletion of gradients, resulting in a state of maximum dissipative behavior of the dissipative structures. One requirement for such dynamics to take place is, of course, that there are sufficient fluxes across the boundary so that the threshold of sediment detachment is achieved, and there needs to be sufficient degrees of freedom so that the structure can arrange in space in an optimum way. This sequence then combines the feedbacks that describe the dynamics with structure formation and thermodynamic limits. It can be formulated in sufficiently general terms that it should apply to the different types of dissipate structures that are found in the Earth system. In this book, this description of structure formation and its relation to dynamic feedbacks and thermodynamic limits remains qualitative and is thus still speculative.

The combination of dissipative structures and their interactions with the boundary conditions of the system can thus provide an extremely powerful theory to understand evolutionary dynamics in general terms. Evolutionary dynamics would reflect the overarching acceleration of the direction imposed by the second law, making dissipative structures more dissipative through the interaction with their boundary conditions and making processes evolve towards their thermodynamic limit. It would allow us to understand the evolutionary target of thermodynamic systems, from atmospheric convection to river networks, terrestrial vegetation, and the Earth system as a whole. The highly complex spatiotemporal organization of processes, as for instance reflected in the structures shown in Fig. 1.4, could explain how a process can reach its thermodynamic limit by forming structures that affect the dissipative behavior of the process. Dissipative structures would then form a central element to understand the emergent, thermodynamic state of the Earth system. In this case, the emergent state of the system can then be predicted by the thermodynamic limit, not because the system is organized in a simple way, but rather the contrary – it is so complex that its emergent state is characterized by the thermodynamic limit. To evaluate the potential of this theory, it requires that processes are linked to each other, particularly regarding their energy-, mass-, and entropy exchange, ultimately up to the planetary radiative forcing. This would then formulate a thermodynamic theory of the whole Earth system that can be evaluated by deriving quantitative estimates that can be tested with observations.

1.6 Connecting Earth system processes

A critical component in formulating thermodynamic limits of Earth system processes and to evaluate the theory just described is to systematically link processes to each other and to include the effects and interactions in the evaluation. These linkages are schematically shown in Fig. 1.5. This picture closely mirrors a view of the Earth system that was already described by Lotka in his book "Elements of physical biology" (Lotka 1925), in which he wrote that:

> "the picture we must keep before us … is that of a great world engine … composed of a multitude of subsidiary units, each separately, and all together as a whole, working in a cycle. It seems, in a way, a singularly futile engine, which … carefully and thoroughly churns up all the energy gathered from the source. It spends all its work feeding itself and keeping itself in repair … ."

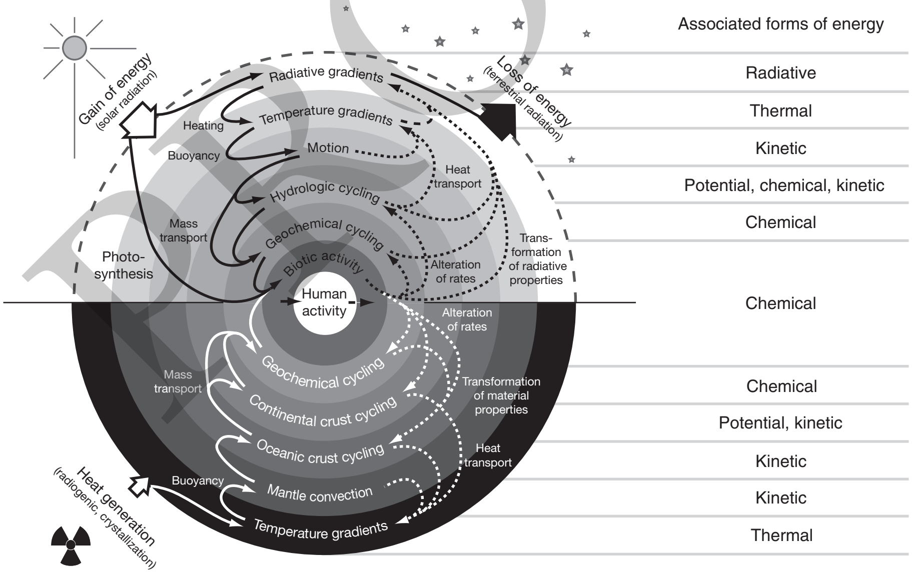

Figure 1.5 A planetary view of the thermodynamic Earth system, with its cascades of energy conversions (left, solid lines), its effects (right, dashed lines), and associated forms of energy shown on the right. The description of this planetary view and the quantification of thermodynamic limits of the conversion rates are the main objectives of this book. Modified from Kleidon (2010, 2012).

The picture shown in Fig. 1.5 embraces Lotka's view. It shows the processes of the surface-atmosphere system (top half) and those of the Earth's interior (bottom half) as well as the two major drivers, solar radiation and interior cooling, of the "great world engine." The first driver results from the spatial and temporal variation in solar radiation at the system boundary. The black arrows in Fig. 1.5 show how this forcing then acts to cause further gradients and dynamics in the system. The gradients in radiative forcing generates uneven heating of the surface, resulting in temperature gradients. These temperature gradients create density differences in the near surface air and buoyancy forces that result in atmospheric motion. Atmospheric motion provides the means to transport water vapor and other constituents. By doing so, it lifts moist air to greater heights, brings the water vapor to condensation and precipitation, so that the descending air is dehumidified. The dehumidification of the atmosphere is associated with gradients that drive evaporation and desalination of the evaporated water at the surface. Thus, atmospheric motion is mostly responsible for maintaining the global hydrologic cycle. The transport of water to land drives river runoff and sediment transport, but also provides the means to chemically dissolve the continental crust, thus driving geochemical cycling of dissolved substances. A similar sequence is shown for interior processes, where heat generation in the interior as well as secular cooling provide the means to generate temperature gradients in the interior. These temperature gradients cause density differences that generate mantle convection, plate tectonics, continental uplift, and thereby the means for the geochemical cycling of material mostly in solid form. Hydrological and geochemical cycling provide the basic resources that feed biotic activity, jointly with the direct utilization of sunlight by photosynthesis. Human activity, in turn, uses the results of biotic activity as food sources. Hence, we get a sequence of transformations from the planetary drivers of solar radiative energy flux and interior cooling down to biotic and human activity.

The linkages between the different processes shown in Fig. 1.5 relate to the different forms of energy that they involve. With radiation and temperature differences, these forms are straightforward and involve radiative energy and thermal energy. Forms of motion are associated with kinetic energy. Hydrologic and geochemical cycling involve different forms of energy, including potential energy, e.g., associated with water droplets in clouds; chemical energy associated with chemical composition, e.g., carbon in different forms such as methane or carbon dioxide; in form of binding energies, such as water bound to a soil matrix; and with kinetic energy, e.g., associated with river flow. Likewise, processes in the interior are associated with different forms of energy. These involve the thermal energy stored in the interior, the kinetic energy associated with the motion of mantle convection and plate tectonics, the potential energy associated with the continental crust, and chemical energy of the geochemical composition. The sequences described here that link the planetary drivers to the different processes within the Earth system are thus intimately linked with energy conversions among the different types of energy. This is where the linkage to thermodynamics comes in as it constrains these rates of energy conversions.

Also shown in Fig. 1.5 are the consequences of the different processes back to the drivers by the dashed arrows. These effects can broadly be understood in terms of altered rates of material transformations, transport of heat, and in terms of altering the radiative properties of the system. To start at the center, biotic activity alters the rates of geochemical and hydrologic cycling and it alters the radiative properties of the surface. A vegetated surface, for instance, is generally darker, thus absorbs more solar radiation, and it can maintain evapotranspiration for longer periods than a bare surface in the same climatic environment. The rates of geochemical cycling in the associated soil are also typically enhanced compared to a bare soil substrate. These altered rates affect the chemical composition of the atmosphere which results in modified radiative properties. Furthermore, hydrologic cycling as well as motion in general involves substantial rates of heat transport, which affects temperature gradients. As temperature is directly linked to the radiative exchange, these effects on temperature gradients affect emission of radiation and radiative gradients. This, ultimately, alters the radiative entropy export to space, the planetary boundary conditions, and the thermodynamic state of the planet.

Thermodynamics applies to these sequences and their effects, and sets firm limits to the magnitude of the associated rates of energy conversions and thus to the overall operation of the "great world engine." By following the planetary forcing down along these sequences, thermodynamic limits allow us to estimate the rates of energy conversions, the associated magnitudes of the fluxes and rates and the constraints on effects, interactions, and feedbacks in the Earth system. We can then use these limits to explore feedbacks and evolutionary directions, evaluate the conditions and consequences of life, and place human activity into the context of the operation of the whole Earth system. The description and quantification of this approach is the main scope of this book.

1.7 Structure of this book

This book describes the thermodynamic foundation to understand the functioning of the Earth system. Thermodynamics in combination with simple formulations are used to describe energy conversions, to estimate the magnitude of these conversions as well as the associated processes, and to illustrate the thermodynamic implications of the resulting dynamics on the thermodynamic state of the Earth system. What this book does not provide is a complete and detailed description of thermodynamics. Here, the reader is referred to introductory physics textbooks (e.g., Feynman et al.

1966), general books on non-equilibrium thermodynamics (e.g., Kondepudi and Prigogine 1998), or specific books on thermodynamics of Earth system processes (e.g., Ambaum 2010; Bohren and Albrecht 1998; Verhoogen 1980). This book focuses on the extent to which thermodynamics is needed to gain a better understanding of how processes operate and interact within the Earth system context and thereby shape the functioning of the whole, thermodynamic Earth system.

The first part of the book provides the basics of thermodynamics that are needed to make this planetary view quantitative: Chapter 2 deals with the different forms of energy and entropy that are associated with Earth system processes. The laws of thermodynamics in the context of the Earth system are described in Chapter 3. The limits that follow from these laws are derived and demonstrated with a few examples in Chapter 4. Chapter 5 contains a general description of the basic feedbacks that are associated with the dynamics that would result in the tendency of natural systems to evolve to their thermodynamic limit.

The second part of the book deals with the formulation of Earth system processes in terms of energy conversions. Radiative exchange is described in Chapter 6 and it is estimated how much energy can maximally be converted from radiation. Chapter 7 starts with the description of buoyancy as the main process that generates motion from a perspective of energy conversions, relates these to the various forms of motion, and estimates the magnitudes of energy conversions involved. In Chapter 8, the hydrologic cycle is related to these energy conversions. Geochemical transformations and resulting cycles as well as life as a biogeochemical process are described in Chapter 9. Chapter 10 sets a special focus on processes on land, where processes are strongly shaped and interact with terrestrial vegetation. This part describes the setting in which most of human activity takes place and where it affects the Earth system most directly. Human activity is then treated to the extent to which it relates to energy conversions in Chapter 11. Each of these chapters closes by placing the particular set of processes back into the overall thermodynamic setting of the Earth system.

This book closes with the integration of the various processes back to the planetary scale and discusses its implications. Chapter 12 summarizes the various energy conversions associated with Earth system processes described in the specific chapters. The synthesis of the thermodynamic foundation of the Earth system is provided by discussing the implications of this view with respect to the topics raised here, specifically regarding the habitability of planetary environments, the evolutionary dynamics of the biosphere and the Earth system, and a sustainable future of the Earth system. It closes with a perspective of how this thermodynamic theory of the Earth can be further developed and what the implications are for Earth system science.