

Available online at www.sciencedirect.com







Physics of Life Reviews 7 (2010) 424-460

www.elsevier.com/locate/plrev

Review

Life, hierarchy, and the thermodynamic machinery of planet Earth

Axel Kleidon

Max-Planck-Institut für Biogeochemie, Hans-Knöll-Str. 10, 07745 Jena, Germany

Received 2 September 2010; accepted 14 September 2010

Available online 12 October 2010

Communicated by J. Fontanari

Abstract

Throughout Earth's history, life has increased greatly in abundance, complexity, and diversity. At the same time, it has substantially altered the Earth's environment, evolving some of its variables to states further and further away from thermodynamic equilibrium. For instance, concentrations in atmospheric oxygen have increased throughout Earth's history, resulting in an increased chemical disequilibrium in the atmosphere as well as an increased redox gradient between the atmosphere and the Earth's reducing crust. These trends seem to contradict the second law of thermodynamics, which states for isolated systems that gradients and free energy are dissipated over time, resulting in a state of thermodynamic equilibrium. This seeming contradiction is resolved by considering planet Earth as a coupled, hierarchical and evolving non-equilibrium thermodynamic system that has been substantially altered by the input of free energy generated by photosynthetic life. Here, I present this hierarchical thermodynamic theory of the Earth system. I first present simple considerations to show that thermodynamic variables are driven away from a state of thermodynamic equilibrium by the transfer of power from some other process and that the resulting state of disequilibrium reflects the past net work done on the variable. This is applied to the processes of planet Earth to characterize the generation and transfer of free energy and its dissipation, from radiative gradients to temperature and chemical potential gradients that result in chemical, kinetic, and potential free energy and associated dynamics of the climate system and geochemical cycles. The maximization of power transfer among the processes within this hierarchy yields thermodynamic efficiencies much lower than the Carnot efficiency of equilibrium thermodynamics and is closely related to the proposed principle of Maximum Entropy Production (MEP). The role of life is then discussed as a photochemical process that generates substantial amounts of chemical free energy which essentially skips the limitations and inefficiencies associated with the transfer of power within the thermodynamic hierarchy of the planet. This perspective allows us to view life as being the means to transform many aspects of planet Earth to states even further away from thermodynamic equilibrium than is possible by purely abiotic means. In this perspective pockets of low-entropy life emerge from the overall trend of the Earth system to increase the entropy of the universe at the fastest possible rate. The implications of the theory are discussed regarding fundamental deficiencies in Earth system modeling, applications of the theory to reconstructions of Earth system history, and regarding the role of human activity for the future of the planet. © 2010 Elsevier B.V. Open access under CC BY-NC-ND license.

Keywords: Gaia hypothesis; Thermodynamics; Atmosphere–biosphere interactions; Evolution; Earth system; Habitability; Holistic theory; Hierarchy; Entropy; Life; Power transfer; Maximum power principle; Maximum Entropy Production; Human impacts; Global change

E-mail address: akleidon@bgc-jena.mpg.de.

 $^{1571\}text{-}0645$ © 2010 Elsevier B.V. Open access under CC BY-NC-ND license. doi:10.1016/j.plrev.2010.10.002

Contents

1.	Life a	nd the Earth system	425		
	1.1.	On the importance of biosphere–atmosphere–geosphere interactions	426		
	1.2.	On the thermodynamics of widespread life within the Earth system	427		
	1.3.	Developing a theory of life within the hierarchical Earth system	427		
	1.4.	Organization of this paper	429		
2.	Basics	of thermodynamic disequilibrium	429		
	2.1.	The first and second laws of thermodynamics	429		
	2.2.	A simple model to illustrate evolution to thermodynamic equilibrium	430		
	2.3.	Maintaining thermodynamic disequilibrium	431		
	2.4.	The first and second laws and the Earth system	432		
3.	Extend	ling thermodynamics to material fluxes	433		
4.	Gradie	ents, power transfer, and thermodynamic disequilibrium	435		
	4.1.	Characterizing thermodynamic disequilibrium	435		
	4.2.	Thermodynamic disequilibrium and emergent dynamics	437		
	4.3.	Power extraction and Carnot efficiency	437		
	4.4.	Maximum extraction of power from a gradient	438		
	4.5.	Using power to drive disequilibrium in the momentum balance	439		
	4.6.	Transferring maximum power to motion	440		
	4.7.	Using motion to perform work	441		
	4.8.	Components for a hierarchy of power transfer	443		
5.	Driver	s of the thermodynamic machinery of planet Earth	443		
	5.1.	Solar radiation	444		
	5.2.	Earth's interior	445		
	5.3.	Celestial bodies	445		
	5.4.	Cosmic radiation	445		
6.	Hierar	chy of power transfer within the Earth system	445		
	6.1.	A hierarchy of power transfer	445		
		6.1.1. Power transfer from solar radiation to atmosphere and surface	446		
		6.1.2. Power transfer from internal heating to mantle and surface	447		
		6.1.3. Aspects omitted from the hierarchy	447		
	6.2.	Coupling of atmosphere–surface–interior processes and life	448		
	6.3.	The global work budget	448		
	6.4.	Maximizing power generation and transfer	450		
	6.5.	Revisiting the Gaia hypothesis	451		
7.	Discus	sion	452		
	7.1.	Limitations	452		
	7.2.	Implications	453		
8.	Synthe	esis and outlook	454		
Ackno	owledge	ements	455		
Appen	ndix A.	Simple momentum balance model	455		
Appendix B. Maximum power of vertical gradients 4					
Appendix C. Maximum power in temporal variations					
Refer	ences .		457		

1. Life and the Earth system

It is now widely accepted that life has substantially transformed the Earth system. This thought – that life is *the* geological force – was introduced by Vernadsky in his seminal work "The Biosphere" [1] many years ago. Some forty years ago, Lovelock [2] described a concrete example for such an effect, the alteration of the atmospheric composition by life, particularly in reference to the unusually high concentration of molecular oxygen in the Earth's atmosphere. This state represents chemical disequilibrium with respect to other constituents of the atmosphere and is unique when

compared to other planetary atmospheres of the solar system. The production of molecular oxygen is directly linked to photosynthetic activity, which reflects the majority of the activity of life on Earth. Photosynthetic activity uses sunlight as an energy source and transforms carbon dioxide and water into chemical free energy in form of carbohydrate and molecular oxygen, which is released into the atmosphere. If oxygen would not be continually replenished by photosynthesis, it would react and the atmospheric composition would reach a final state of thermodynamic equilibrium. Lovelock argued that therefore the observed disequilibrium in the atmospheric composition was due to the presence of life and is thus an unmistakable sign of a planet with widespread life.

Disequilibrium is not confined to atmospheric composition, but can be observed with respect to many other variables. For instance, a redox gradient developed between the Earth's oxidizing atmosphere and the reducing crust through time [3], which is depleted by geochemical reactions. Topographic gradients develop, from the mountain tops to the sea floor [4] that are continuously depleted by erosion and sediment transport. How are these gradients maintained? Does life contribute to maintaining these disequilibrium states?

In this paper I extend Lovelock's perspective of thermodynamic disequilibrium and life to processes of the whole Earth system as well as their interactions in order to develop a holistic theory of life in the Earth system. To do so, I formulate Earth system processes in general thermodynamic terms. This then will allow us to calculate disequilibrium with many more variables and understand the driving forces for such disequilibrium states. Such a theory then allows us to quantify the effect of life on the driving forces of planetary disequilibrium states. As we will see, interactions play a central role in this theory, as does thermodynamics. These two important components are further motivated before I describe the outline of this paper.

1.1. On the importance of biosphere-atmosphere-geosphere interactions

With the generated chemical free energy by photosynthesis, organisms can perform the work to build persistent structures. Plants, for instance, build leaves, stems, and roots. These persistent structures, in turn, enhance the ability to absorb solar radiation and – on land – enable trees to reach water deep in the soil. With this, organisms affect the extent to which incoming solar radiation is absorbed and the rate at which precipitated water is transpired back into the atmosphere, both affecting the prevailing environmental conditions surrounding the organisms. Furthermore, these two examples affect the environmental conditions of the photochemical machinery of the organisms (e.g. the leaf temperature through the latent heat of water) but also the environmental conditions at large (in terms of the water vapor concentration in the atmosphere).

Merely these two physical effects – the increased absorption of solar radiation at the surface and the increased ability to recycle water to the atmosphere in the presence of terrestrial vegetation can already substantially modify the physical environmental conditions. At the local scale, these differences can be felt on a hot summer day when comparing the cool, moist air in a forest to the hot and dry conditions of a parking lot. At larger scales, these effects modulate temperature and continental moisture recycling, as for instance demonstrated by extreme climate model simulations of a "green planet" – a world where rainforests were planted everywhere on land – and a "desert world", in which the effects of terrestrial vegetation were removed [5]. When evaluated in terms of what these contrasting physical conditions imply for biotic activity, it was found that the conditions of the "green planet" as well as for the present-day allow for substantially higher productivity [6]. Such self-enhancing effects could be understood in evolutionary terms as a result of a "feedback on growth" [7].

In addition to these physical effects, life alters the chemical environment on Earth, resulting in biogeochemical effects and feedbacks. By altering the chemical composition of the atmosphere, life affects the strength of the greenhouse effect and thereby surface heating. On long time scales, life has substantially altered weathering rates of silicate rocks [8], for instance by enhancing the acidity of water in the soil, enhancing the substrate surface area, and by effects on the hydrologic cycle. An enhancement of weathering rates affect the geologic carbon cycle by drawing down atmospheric CO_2 concentrations. Furthermore, the emergence of photosynthesis has been suggested to have led to the formation of continents [9] by driving chemical disequilibrium in the seawater.

These examples are only a few of the many effects by which life alters the environment, which in turn alter the abiotic conditions in which life operates. Hence, we deal with atmosphere–biosphere and geosphere–biosphere interactions. These interactions take place on time scales of seconds (e.g. leaf temperature) to the lifetime of the planet (e.g. formation of continents). Depending on how strong these interactions are and on their relative importance, these should be critical to understand the present-day conditions of Earth, life, and its past co-evolution [10]. How we would quantify the relative importance of biotic processes on the environment in general terms is, however, unclear. In this paper I explore biotic processes in terms of their role in driving thermodynamic disequilibrium, which should give us a quantitative and fundamental basis for evaluating the importance of life on the planetary environment.

1.2. On the thermodynamics of widespread life within the Earth system

With the notion of atmosphere–biosphere–geosphere interactions nowadays being relatively well accepted, we can move on and ask more fundamental questions on the nature of these interactions and why they are likely to emerge within the complex Earth system. Why does life modify the environment in the way it does? Are biotic effects just random, a historical coincidence, or do they act in a particular direction? How can we reconcile individual examples of biotic influences with possibly fundamental trends that describe the functioning of the whole Earth system and how it evolves through time?

One fundamental theory in physics that allows us to address these questions is thermodynamics. Central to thermodynamics are the first and second laws. While the first law of thermodynamics quantifies how much work can be extracted from gradients in heating and cooling under the constraint of energy conservation, the second law tells us about the irreversibility of processes and thereby provides us with an "arrow of time" [11]. Most common applications of thermodynamics are usually found in engineering, for instance the typical applications to the Carnot cycle of heat engines and refrigerators. Thermodynamics has also been applied to physical processes of the Earth system, e.g. the generation and dissipation of atmospheric motion [12] and associated optimality [13–15], the intensity of hurricanes [16], hydrological processes at the land surface [17,18], the atmospheric branch of hydrologic cycle [19,20], ocean dynamics [21,22], and, obviously, geochemical transformations. These processes generally operate away from a state of thermodynamic equilibrium and there is some evidence that these operate in steady states at which they maximize their dissipative activity, or, almost equivalently, maximize power generation or entropy production (the proposed Maximum Entropy Production (MEP) principle, [23–27]).

As noted by Boltzmann [28] and Schroedinger [29], thermodynamics must apply to the living organisms as well. Life feeds on low entropy "food" and rejects high entropy "waste" products and heat, thereby fueling its metabolism and sustaining its structure. Living organisms, just as any other dissipative process, maintain their state away from thermodynamic equilibrium by an overall net export of entropy to the surroundings. This commonality of living organisms and purely physical dissipative processes led Lovelock and Margulis [30] to use the metaphor of describing Earth as a superorganism. To characterize the organization of the steady state that describes the sum of all living organisms, in an ecosystem at the small scale, or in the biosphere at the global scale, the same thermodynamic maximization principles have been proposed, first by Lotka [31,32], and further explored by others [33–39].

What has been mostly absent is to integrate these components into one big picture of the whole planet. Thermodynamics is the natural choice for the language to describe such a picture, since the formulations of thermodynamics are so general that they allow us to describe all Earth system processes using the same terminology. When doing so, we can understand the interactions among Earth system processes and life and relate it to the extent to which the system is maintained away from thermodynamic equilibrium. Applying thermodynamic organizational principles, such as maximum power or MEP, to these interactions could help us to better understand how the whole Earth system behaves in steady state, how regulatory mechanisms and feedbacks play out. This then should help us to better relate planetary habitability to thermodynamic constraints and disequilibrium at various levels and extend Lovelock's vision of the habitable Earth system.

1.3. Developing a theory of life within the hierarchical Earth system

Here I relate life and the thermodynamic state of planet Earth by developing a theory of the whole Earth system that is based on non-equilibrium thermodynamics. This theory develops a hierarchical view of Earth system processes in which processes generate free energy, dissipate, but – most importantly – transfer power from one process to other processes higher up in the hierarchy, from radiative exchange to motion to geochemical cycling. Thermodynamics, specifically the first and the second laws, set the rules for operating these power transfer processes, maximum rates of power generation and transfer, and on how these processes interact. Characteristic maximum transfer rates should exist, as formulated by the maximum power principle (or, closely related, MEP), setting upper bounds on how much power can be transferred among processes.



Fig. 1. Illustration of the formation of a hierarchy based on power transfer. A radiative gradient drives the atmospheric heat engine (top figure). This heat engine, which acts like a motor (indicated by the "M"), can drive other processes out of equilibrium, as indicated by the "belt" around the motor. Shown here is the connection to the global hydrologic cycle, where the atmospheric motor drives the dehumidifier and thereby the hydrologic cycle. The hydrologic cycle, with its net transport of water from oceans to land can be seen as another motor that drives continental runoff. This, in turn, acts as a motor to transport rock material in suspended and dissolved form from land to ocean.

An example of this hierarchical view is shown in Fig. 1. Radiative fluxes at the Earth–space boundary lead to spatial and temporal differences in radiative heating and cooling. The resulting temperature differences fuel the heat engine that generates motion within the atmosphere, as symbolized by the engine symbol in the figure. The kinetic energy inherent in the flow lifts moist air, cools it, brings it to saturation, condensation and precipitation, thereby acting to remove water from the atmosphere. Thereby the atmospheric heat engine drives the atmospheric dehumidifier as indicated by the "belt" around the engine symbol in the figure. This dehumidifier acts as another engine that drives the global cycling of water. The hydrologic cycle brings water to land at a higher elevation than the sea level, which enables continental runoff to drive the transport of dissolved ions and sediments to the sea floor. This "transporter" of continental mass interacts with interior processes of the global rock cycle and results in the geochemical cycling of rock-based elements.

The emergent dynamics of this hierarchy, and specifically the resulting extent of chemical disequilibrium, is strongly governed by how much power is transferred among each of the processes since dissipative processes will inevitably act to slow down the engines and result in inefficiencies. Because of the inevitable inefficiencies at each of the transfer processes, abiotic processes can only drive and maintain states of chemical disequilibrium to a relatively small extent. Photosynthetic life, in contrast, is able to directly tap into the power contained in the flux of solar radiation, skips the myriad of inefficiencies contained in abiotic power transfer processes, and is thus able to drive and maintain substantial chemical disequilibrium states. Hence life is of central importance in driving and maintaining planetary disequilibrium.

Using thermodynamics we should be able to quantify the extent to which life contributes to disequilibrium. To do so, we need to first understand the power transfer in the dominant hierarchy of Earth system processes that is associated with geochemical cycling as well as the power that drives this hierarchy. We then need to estimate the power associated with biotic activity and compare this power to the power involved in abiotic geochemical processes. This will then result in a holistic, thermodynamic description of life within the Earth system, in which the thermodynamic nature of interactions among processes and associated maximum power states play a central role in the functioning of the whole Earth system.

1.4. Organization of this paper

The paper is organized to provide the background on the important building blocks and their quantitative illustration for developing this hierarchical theory. The basis for this theory is non-equilibrium thermodynamics as it applies to Earth system processes. The background on thermodynamics and the natural trend towards states of thermodynamic equilibrium is explained and illustrated in the following Section 2. I then show that the basics of thermodynamics can be extended to practically all types of variables that characterize gradients in the Earth system in Section 3. In Section 4 I show how gradients are created by transferring power into the system, thereby allowing work to be performed within the system. The import and transfer of power allows the maintenance of states away from thermodynamic equilibrium and to drive processes that act to deplete the overall driving gradients at a faster rate. Hence, the overall effect of this hierarchy is to enhance the overall rate of entropy production, resulting in the fastest approach to thermodynamic equilibrium that is possible at the planetary scale. Furthermore, characteristic maximum rates exist with which power can be extracted from a gradient to create other gradients. This maximization of power is related to the proposed principle of Maximum Entropy Production (MEP).

I then use this conceptual view to describe the relevant Earth system processes including life in such a hierarchical view in Section 6. The resulting rates at which work is performed at different levels of this hierarchy are estimated to provide a global work budget. Together with the global energy and entropy budget, this global work budget completes the description of the Earth system in terms of the first and second laws. The implications of maximum power transfer for Earth system functioning is discussed. The role of life, particularly photosynthetic life, is discussed in terms of altering power transfer and thereby the structure and strength of this hierarchy. The resulting view of the Earth system is then compared to the Gaia hypothesis of James Lovelock [40,41,30] and the role of human activity in the global work budget is being discussed.

This thermodynamic theory is, of course, a first sketch, with some limitations and missing details, but also with profound implications. These implications potentially range from more basic topics of understanding Earth system feedbacks and reconstructing the Earth's history to more applied topics of how we should model the Earth system and how the future of humans should look like. These are discussed in Section 7. I close with a brief summary and conclusion. The details of the models used here for illustration are provided in Appendices A–C.

2. Basics of thermodynamic disequilibrium

I first review the basics of classical thermodynamics and illustrate with a simple model how an isolated system evolves to a state of thermodynamic equilibrium. I then generalize the means to get to thermodynamic equilibrium to a range of variables relevant to Earth system processes.

2.1. The first and second laws of thermodynamics

The first and second laws are the foundation of thermodynamics and provide the quantitative basis of thermodynamic evaluations. The first law relates changes of energy content and heat fluxes to the amount of work that can be done by the system. It states that the change of internal energy dU of the system is balanced by the exchange of heat dQ with its surroundings and the work done by the system dW:

$$dU = dQ - dW \tag{1}$$

The convention here is that dW > 0 if the work is done by the system, and dW < 0 if work is done on the system by the surroundings.

All processes follow the direction given by the second law. This law states that the entropy S of an isolated system can only increase with time, i.e. $dS \ge 0$. For small changes, the change of entropy dS as a result of the addition or removal of a small amount of heat dQ at a temperature T is given by:

$$dS = \frac{dQ}{T} \tag{2}$$

To illustrate how Eq. (2) results in an increase of entropy and hence the second law, I use the simple example of transferring heat from a hot to a cold reservoir. A small amount of heat dQ is removed from a hot reservoir

a. 2-box model



Fig. 2. Simple two-box model to illustrate the evolutionary trend towards a state of maximum entropy of an isolated system. The entropies S_h , S_c and S_{tot} are expressed as a fraction of the value representing thermodynamic equilibrium. The parameter values and initial conditions were chosen to resemble conditions similar to those found on Earth. For the parameter c, a value of $c = 2 \cdot 10^8$ J m⁻² K⁻¹ was used, which roughly corresponds to the heat capacity of 50 m oceanic mixed layer. The initial temperatures were set to roughly represent the radiative equilibrium temperatures of the tropics and extratropics for present-day conditions on Earth of $T_{h,0} = 311.9$ K and $T_{c,0} = 267.6$ K. After [26].

of temperature T_h and added to a cold reservoir of temperature T_c . The entropy of the hot reservoir is reduced by $dS_h = -dQ/T_h$ while the entropy of the cold reservoir, once the added heat is fully mixed within the reservoir, is increased by $dS_c = dQ/T_c$. Hence, the total entropy produced by transferring heat dQ from hot to cold is:

$$dS_{tot} = dS_h + dS_c = dQ \cdot \left(\frac{1}{T_c} - \frac{1}{T_h}\right)$$
(3)

Since $T_c < T_h$, $dS_{tot} > 0$ and the process of transferring heat is irreversible, it produces entropy, it acts to deplete the gradient $T_h - T_c$, and it acts to bring the system closer to a state of thermodynamic equilibrium in which $T_h = T_c$.

2.2. A simple model to illustrate evolution to thermodynamic equilibrium

The second law, entropy production, and the natural tendency of the system to evolve to a state of thermodynamic equilibrium is illustrated with a simple model (Fig. 2). This model consists of two heat reservoirs of different initial heat contents (with equal heat capacity c, and temperatures T_h and T_c respectively). These two reservoirs exchange heat with each other, but are isolated to the surroundings. Expressing the heat flux between the boxes as $J_{heat} = dQ/dt$ (with a positive flux directed from T_h to T_c), we have two simple differential equations that describe the evolution of the temperatures of the heat reservoirs with time:

$$c \cdot \frac{dT_h}{dt} = -J_{heat}, \qquad c \cdot \frac{dT_c}{dt} = J_{heat} \tag{4}$$

where the heat flux J_{heat} can be expressed as $J_{heat} = k \cdot (T_h - T_c)$ with k being a conductivity and fluxes being expressed in units of W m⁻² in the following.

The respective entropies of the system S_h , S_c and S_{tot} are described by the entropy budgets of the hot and cold reservoirs respectively:

$$\frac{dS_h}{dt} = -\frac{J_{heat}}{T_h}, \qquad \frac{dS_c}{dt} = \frac{J_{heat}}{T_c}$$
(5)





Fig. 3. Simple two-box model (as in Fig. 1) to illustrate the maintenance of disequilibrium in a non-isolated system resulting from entropy exchange at the system boundary. The entropies S_h , S_c and S_{tot} are expressed as a fraction of the value representing thermodynamic equilibrium. For the parameter k, a value of $k = 1 \text{ W m}^{-2} \text{ K}^{-1}$ was used. After [26].

and

$$\frac{dS_{tot}}{dt} = \frac{dS_h}{dt} + \frac{dS_c}{dt} = J_{heat} \cdot \left(\frac{1}{T_c} - \frac{1}{T_h}\right) = \sigma_{heat} \tag{6}$$

so that the increase of the total entropy of the two-box system equals the total amount of entropy produced σ_{heat} by the heat exchange process within the system.

The numerical integration of the model is shown in Fig. 2. It clearly shows how the initial temperature gradient $T_h - T_c$ is depleted by the flux J_{heat} in time. This trend is reflected in the decrease in entropy production σ_{heat} in time. Initially, the warm box stores more heat and has hence a higher entropy than the cold box. The heat flux J_{heat} depletes the entropy of the hot reservoir and by adding heat to the cold reservoir, entropy is increased in that box. Due to the mixing of the heat contents, the increase of entropy in the cold reservoir is greater than the reduction of entropy in the hot reservoir. Hence, the overall entropy of the system S_{tot} increases with time.

2.3. Maintaining thermodynamic disequilibrium

When entropy exchanges are allowed for at the system's boundary, the system can be maintained away from a state of thermodynamic equilibrium. Fig. 3a shows a setup that resembles a case with entropy exchanges of both boxes with the surroundings. While this setup is not the simplest possible, this setup is chosen because it is used later to describe the differential heating of the Earth between the tropics (warm box) and the poles (cold box).

To account for energy and entropy exchange across the system boundary, we need to alter the energy balances of the simple system considered before (Eqs. (4) and (5)) to:

$$c \cdot \frac{dT_h}{dt} = J_{in,h} - J_{out,h} - J_{heat}, \qquad c \cdot \frac{dT_c}{dt} = J_{in,c} - J_{out,c} + J_{heat}$$
(7)

and

$$\frac{dS_h}{dt} = \frac{J_{in,h}}{T_{in}} - \frac{J_{out,h}}{T_h} - \frac{J_{heat}}{T_h} + \sigma_{mix,h}, \qquad \frac{dS_c}{dt} = \frac{J_{in,c}}{T_{in}} - \frac{J_{out,c}}{T_c} + \frac{J_{heat}}{T_c} + \sigma_{mix,c}$$
(8)

where the entropy associated with the incoming energy is associated with a characteristic temperature T_{in} . In this setup entropy is being produced by the mixing of the incoming energy fluxes $J_{in,h}$ and $J_{in,c}$ in the two boxes at temperatures T_h and T_c respectively:

$$\sigma_{mix,h} = J_{in,h} \cdot \left(\frac{1}{T_h} - \frac{1}{T_{in}}\right), \qquad \sigma_{mix,c} = J_{in,c} \cdot \left(\frac{1}{T_c} - \frac{1}{T_{in}}\right) \tag{9}$$

and by the mixing associated with heat flux J_{heat} from the warm box to the cold box, as before:

$$\sigma_{heat} = J_{heat} \left(\frac{1}{T_c} - \frac{1}{T_h} \right) \tag{10}$$

The entropy budget of the whole system is given by:

$$\frac{dS_{tot}}{dt} = \frac{dS_h}{dt} + \frac{dS_c}{dt} = \sigma_{mix,h} + \sigma_{mix,c} + \sigma_{heat} - NEE$$
(11)

where $NEE = (J_{out,h}/T_h + J_{out,c}/T_c) - (J_{in,h} + J_{in,c})/T_{in}$ is the net entropy exchange across the system boundary.

What we notice in Fig. 3 is that the initial gradient in temperature is depleted as in the previous setup, but it does not vanish in the steady state. Instead, a non-zero heat flux transports heat from warm to cold that acts to deplete the temperature gradient that is continuously built up by the differential heating $J_{in,h} - J_{in,c}$. This heat flux produces entropy by the depletion of the temperature gradient, but instead of increasing the entropy of the system to the maximum, the produced entropy in steady state is exported by the enhanced export of entropy associated with the outgoing heat flux $J_{out,h} + J_{out,c}$. The enhanced entropy export results from the overall lower temperature at which the total amount of received heat is exported to the surroundings.

2.4. The first and second laws and the Earth system

When applied to the Earth system, the terms of the first and second laws are mostly captured by the global energy balance and the global entropy budget. These budgets are shown in combined form in Fig. 4.

The first law is represented mostly by the global energy balance, in which the net heating and cooling rates and heat fluxes describe the dQ (or J = dQ/dt) term of the first law. Note that the dW term is absent in the discussion of the global energy balance, as it describes a separate global work budget. This budget plays a critical role for driving the dynamics of the system and its interactions, and we will focus on this budget later in this paper. The dominant heating term in this budget is the absorption of sunlight at the Earth's surface. About 40% of the surface heating is lost by net emission of radiation from the surface, while the other 60% are transferred to the atmosphere by the sensible and latent heat flux. Both heat fluxes are closely associated with turbulent processes in the boundary layer, even though frictional dissipation by these turbulent processes is notably smaller than the associated turbulent heat fluxes. Heat exchange with the interior only plays a minor role.

The global entropy balance describes the dS (or $\sigma = dS/dt$) terms of the second law. The estimates shown in Fig. 4 are mostly derived from heat fluxes and their respective temperature gradients and are taken from previous estimates [42–44]. The dominant dissipative process is the absorption of solar radiation at Earth's much lower temperatures of about 280 K compared to the emission temperature of the Sun of about $T_{sun} = 5760$ K. Entropy production by absorption contributes more than 90% to the planetary entropy production of about 918 mW m⁻² K⁻¹. The remaining < 10% are produced by dissipative processes associated with the scattering of direct solar radiation into diffuse radiation (i.e. by enlarging the solid angle, see e.g. [42] for details), hydrologic cycling with phase transitions occurring at different temperatures, frictional dissipation of motion, diffusion of heat in and out of the ground at different temperatures, carbon cycling that is fueled the utilization of sunlight by photosynthesis and, a very minor component, by processes of the Earth's interior.

The entropy budget could, in principle, be provided in much greater detail. Material diffusive fluxes in the atmosphere, for instance water vapor, degrade gradients in concentration, thereby also producing entropy. To express entropy production of these terms requires formulating the fluxes in terms of thermodynamic variables of the material characteristics. The basis for such a quantification is provided in the next section.



Fig. 4. The global budgets of energy and entropy. Arrows represent fluxes of energy, and boxes represent dissipative processes. Fluxes J are given in units of W m⁻², associated temperatures T in K, solid angle Ω in radians, and entropy production σ in mW m⁻² K⁻¹. After [26] with numbers based on [42–44].

3. Extending thermodynamics to material fluxes

Irreversibility and resulting entropy production results not only from mixing of heat, but is a common characteristic for most Earth system processes. The expression for entropy production used above (Eq. (10)) is based on variables that characterize heat content (temperatures T_h and T_c) and heat transport (flux J_{heat}). Heat is only one, though dominant form of energy that contributes to the total internal energy of a system U. Other forms of energy can be expressed in terms of pairs of conjugated variables that taken together express other forms of energy. Each pair combines an "intensive" variable (i.e. independent of the size of the system) with an "extensive" variable (which depends on the size of the system). Such pairs of conjugated variables that are relevant to Earth system processes are summarized in Table 1 and associated, irreversible processes relevant to the Earth system are illustrated in Fig. 5. The formulations for entropy production for these material processes are described qualitatively in the following. For a more in-depth treatment, the reader is referred to reviews [23,25] and books on non-equilibrium thermodynamics [45,24].

Examples for contributions to internal energy that is not related to heat and the associated pairs of conjugated variables include pressure p and volume V (associated with pressure–volume work), velocity \vec{v} and momentum $\vec{p} = \rho \vec{v}$ (with density ρ) that express kinetic energy, gravitational potential $\phi = gz$ (with z being the height with respect to some reference height) and mass m yield potential energy, chemical potential μ and mass m express energy stored in concentrations of chemical compounds or binding forces (such as capillary and adhesive forces) and chemical affinity

A selection of different forms of energy within the Earth system and its associated conjugated variables

A selection of unreferit forms (in energy within the Earth system and its associated	conjugated variables.
Form of energy	Intensive variable (independent of system size)	Extensive variable (dependent on size of system)
Heat	Temperature T	Entropy S
Mechanical energy	Pressure p	Volume V
Geopotential energy	Gravitational potential ϕ	Mass m
Kinetic energy	Velocity \vec{v}	Momentum \vec{p}
Chemical energy	Chemical potential μ Chemical affinity A	Mass <i>m</i> Extent of chemical reaction ξ



Fig. 5. Qualitative illustration of different processes within the Earth system and their relation to depleting gradients, thereby bringing different variables to states of thermodynamic equilibrium.

A and the extent of chemical reactions ξ describe the energy in a given state of chemical reactions. Other forms not listed here (and not further explored in the following) are for instance stress and strain and electromotive force and electrical charge.

A change dU in the total energy of the system can then be expressed as the sum of changes in each of the contributions:

$$dU = T dS + p dV + \phi dm + \vec{v} \cdot d\vec{p} + \sum_{i} \mu_i dm_i + \sum_{j} A_j d\xi_j$$
(12)

where the sums run over different physical states (solid, liquid, gas) and/or chemical compounds. But even in the absence of a change in U, gradients in any of these pairs of conjugated variables can exist and be used in the context

Table 1

$$dA = dU - T \, dS \tag{13}$$

This is, of course, a simplified expression in that the terms that contribute to the free energy within a system are not independent from each other when considered in an Earth system context. Ultimately, practically all forms of free energy are generated directly or indirectly by differences in heating, either by absorption of solar radiation, or by heating within the inner Earth (exceptions to this are initial conditions e.g. in chemical energy, and tidal forces by celestial bodies that perform work as well). Depleting these gradients in heating then allows for the generation of other gradients and thus generates free energy. For instance, gradients in heating result in a temperature gradient ∇T that may result in pressure gradients ∇p that are used to perform the work to generate velocity gradients ∇v (i.e. motion). The mass transport associated with motion then acts to deplete the pressure gradient, and the associated heat transport depletes the gradient in heating. Likewise, gradients in geopotential $\nabla \phi$ (e.g. mountain slopes) perform work to generate motion (e.g. stream flow of rivers) that is used to deplete the geopotential gradient (e.g. by fluvial erosion).

The extension of thermodynamics to material fluxes by using the notion of conjugated variables is essential for this paper as it is the basis to formulate the fundamental, thermodynamic constraints of the drivers of the Earth system, the limits on the emergent dynamics, reformulates the interactions between processes in terms of power generation and free energy dissipation, and it sets the limits of chemical free energy generation and disequilibrium. The next step is to revisit the first and second laws as the accounting rules that determine the limits on the ability to transform a gradient in one set of conjugated variables into gradients of another set of conjugated variables, thereby causing thermodynamic disequilibrium at different levels within a hierarchy of transformations.

4. Gradients, power transfer, and thermodynamic disequilibrium

So far it was explained how various types of gradients within the Earth system are depleted by irreversible processes, following the second law of thermodynamics. I now use the first and second laws to show that gradients in a certain thermodynamic variable are formed by continuously performing work on this variable, i.e. by transferring power. This results in the generation of free energy and the resulting disequilibrium can be expressed by an entropy that is related, but not identical to the entropy discussed above. These concepts are then applied to the simple model of the previous section to demonstrate their use.

We then use the simple model shown in Fig. 3 to show that a maximum level of power can be extracted from the gradient in heating. Another simple model of the momentum balance is set up to show how the transfer of power results in a gradient in momentum and a state of thermodynamic disequilibrium with respect to momentum. By combining these two models, it is then shown that the maximum transfer of power from a heat gradient results in maximum thermodynamic disequilibrium with respect to show that thermodynamic disequilibrium with respect to motion. Furthermore, a simple model is then used to show that thermodynamic limits set again a maximum in the rate at which power can be extracted from motion. These models will illustrate how one process drives another out of equilibrium, forming the building block towards a hierarchical view of Earth system processes.

4.1. Characterizing thermodynamic disequilibrium

While a temperature difference in the simple example shown in Fig. 3 is maintained in a steady state of thermodynamic disequilibrium, the value of S_{tot} is not synonymous with disequilibrium per se because it also reflects the total heat content of the system. To better distinguish between these two factors, we combine the definition of entropy (Eq. (2)) with the first law (Eq. (1)) and express a change of the total entropy of the system S_{tot} as:

$$dS_{tot} = \frac{dU + dW}{T} \equiv dS_{heat} + dS_{diseq}$$
(14)

This reformulation expresses the change in dS_{tot} as the sum of entropy change due to changes dU in the total energy content of the system $dS_{heat} = dU/T$ and an additional term $dS_{diseq} = dW/T$ that reflects the amount of work dW done by or on the system that is associated with a state of disequilibrium. Another way to look at this separation into



Fig. 6. Helmholtz free energy A (solid line) and disequilibrium S_{diseq} (dotted line) for the simple models shown in Figs. 2 and 3.

two terms is to separate the contribution of heat to the internal energy from the other types of free energy, such as kinetic energy, potential energy, etc. Note that in a state of thermodynamic equilibrium $dS_{diseq} = 0$ since no work can be performed by the system.

This expression of disequilibrium is directly related to the amount of Helmholtz free energy A within the system (cf. Eq. (13)). When considering changes in time, Eq. (14) becomes:

$$\frac{dS_{tot}}{dt} = \frac{dS_{heat}}{dt} + \frac{dS_{diseq}}{dt} = \frac{1}{T} \cdot \left(\frac{dU}{dt} + \frac{dW}{dt}\right)$$
(15)

Using the change of free energy in time, dA/dt (assuming a fixed temperature):

$$\frac{dA}{dt} = \frac{dU}{dt} - T \cdot \frac{dS_{tot}}{dt} = -T \cdot \frac{dS_{diseq}}{dt}$$
(16)

we notice that the dissipation of free energy A is directly proportional to the depletion of disequilibrium as expressed by S_{diseq} . This analysis is illustrated in Fig. 6 for the simple model used in Figs. 2 and 3.

To describe the temporal behavior of A and S_{disea} further, we write the dynamic equations for these variables as:

$$\frac{dA}{dt} = P_{in} - D \tag{17}$$

and

$$\frac{dS_{diseq}}{dt} = -\frac{P_{in}}{T} + \sigma \tag{18}$$

where P_{in} is the power imported into a process to generate free energy and drive disequilibrium, D is the dissipation rate of free energy, and $\sigma = D/T$ the entropy produced by the dissipation of free energy. When we name $P_{in} - D$ the net work done dW_{net}/dt on a thermodynamic variable

$$\frac{dW_{net}}{dt} = P_{in} - D \tag{19}$$

then the resulting steady state value of the free energy A_{∞} (and disequilibrium, $S_{diseq,\infty}$) can be seen as being the result of the total net work done on the variable in the past, since

$$A_{\infty} = \int_{0}^{A_{\infty}} dA = \int_{0}^{\infty} (P_{in} - D) dt = \int_{0}^{\infty} \frac{dW_{net}}{dt} dt$$
(20)

If we assume that dissipation is proportional to the amount of free energy in the system, i.e. $D = A/\tau$, and assume that $P_{in} \approx const.$, then the dynamics are governed by a simple differential equation of the form:

$$\frac{dA}{dt} = P_{in} - \frac{A}{\tau} \tag{21}$$

The steady state values for free energy A_{∞} and disequilibrium $S_{diseq,\infty}$ are then simply expressed as:

$$A_{\infty} = P_{in} \cdot \tau, \qquad S_{diseq,\infty} = \frac{P_{in} \cdot \tau}{T}$$
(22)

In summary, these simple considerations show that thermodynamic disequilibrium is the result of net work done on a thermodynamic variable. The net work done in turn reflects the combination of the rate of power input P_{in} and a dissipation time scale τ .

4.2. Thermodynamic disequilibrium and emergent dynamics

Thermodynamic disequilibrium can be linked to macroscopic dynamics due to classical forces by using the concept of the entropic force. An entropic force is defined as an emergent force resulting from collective behavior that results from the evolutionary trend towards a state of maximum entropy. An expression of the entropic force F is derived from equating the work done by that force F over a distance dx (as in Newtonian mechanics) to the increase in entropy T dS:

$$dW = \vec{F} \cdot d\vec{x} = T \, dS \tag{23}$$

In other words, the force results in dynamics that dissipate the gradient in entropy and results in a slight amount of dissipative heating, which increases the entropy of the system.

We can use Eq. (23) to express a force as a result of spatial gradients in entropy (dS/dx). When this force is considered per unit time, we get:

$$D = T \cdot \frac{dS_{diseq}}{dt} = \vec{F} \cdot \vec{v}$$
⁽²⁴⁾

where $\vec{v} = dx/dt$.

Likewise, the power to drive disequilibrium in the first place can be expressed equivalently, although then the force results from a gradient in some other thermodynamic variable. It is important to note that most forces that cause and deplete motion, transport, and transformations within the Earth system can be seen as such entropic forces.

4.3. Power extraction and Carnot efficiency

In the following, we will develop examples to demonstrate how power is extracted from one thermodynamic gradient and can be used to drive another thermodynamic variable out of equilibrium. I start with the common derivation of the Carnot efficiency of a thermodynamic process driven by heat extraction from a gradient. While the Carnot efficiency is well known, the following brief derivation is important in that it illustrates the inherent assumptions that results in the expression for the Carnot efficiency. This, in turn, is the basis to understand why the maximum efficiency of natural processes is generally much smaller than the Carnot efficiency.

Instead of considering infinitesimal changes (as in Eq. (1)), I consider these changes per unit time dt, so that the term relating to work dW in the first law becomes extracted power $P_{ex} = dW/dt$. I consider a system with an influx of heat J_{in} that maintains a reservoir at temperature T_h , and an outflux of heat J_{out} of another reservoir with temperature T_c . For this case the first law tells us that

$$\frac{dU}{dt} = 0 = \frac{dQ}{dt} - P_{ex} = J_{in} - J_{out} - P_{ex}$$
(25)

where the extracted power P_{ex} is equal to the heat flux extracted from the system, i.e. $J_{ex} = P_{ex}$. The second law constrains the amount of power that can be extracted from the system by demanding that the net entropy exchange of the system is non-negative. The maximum power is extracted when no irreversible process takes place, hence no entropy is produced within the system and NEE = 0, i.e.:

$$\frac{dS}{dt} = 0 = \sigma - NEE = \frac{J_{in}}{T_h} - \frac{J_{out}}{T_c}$$
(26)

Using Eq. (25) to express J_{out} as $J_{out} = J_{in} - P_{ex,max}$, we get:

$$NEE = 0 = \frac{J_{in}}{T_h} - \frac{J_{in} - P_{ex,max}}{T_c}$$
(27)

or

$$P_{ex,max} = J_{in} \cdot \frac{(T_h - T_c)}{T_h}$$
⁽²⁸⁾

This is the common expression for the Carnot efficiency $\eta = \Delta T / T_h$. Note, however, that the derivation of the Carnot efficiency does not account for: (i) the depletion of the gradient by the heat extraction, (ii) competing processes that may take place within the system that inevitably produce entropy, and (iii) the dissipation of power that results in an additional heating term in the energy balance. For instance, to drive thermal convection, power is extracted from a temperature gradient in the presence of diffusive and radiative heat transport. These two latter processes also deplete the temperature gradient. So when this competition with other processes is taken into account, less power should be extractable from the system.

4.4. Maximum extraction of power from a gradient

To derive an expression for the maximum rate at which power can be extracted from a temperature gradient when the gradient is depleted by the flux and by including competing processes, I use the model described in Section 2.3. To get a comparable expression to Eq. (28), we use the steady state assumption, $P_{ex} = D$, and then get P_{ex} from $\sigma \cdot T_c$:

$$P_{ex} = J_{heat} \cdot \frac{T_h - T_c}{T_h} \tag{29}$$

To simplify the following expressions, I use $\Delta J_{in} = J_{in,h} - J_{in,c}$, $\Delta J_{out} = J_{out,h} - J_{out,c}$, express $J_{out} = J_0 + k_b T$, so that $\Delta J_{out} = k_b \cdot (T_h - T_c)$. Subtracting the steady-state forms of the energy balances (Eqs. (7)) yields $\Delta J_{in} - \Delta J_{out} - 2J_{heat} = 0$. Taken together, these yield for the power:

$$P_{ex} = \frac{J_{heat} \cdot (\Delta J_{in} - 2J_{heat})}{k_b \cdot T_h}$$
(30)

I neglect the dependence of T_h on J_{heat} and find the optimum value for the heat flux $J_{heat,opt}$ that maximizes the extracted power by $dP_{ex}/dJ_{heat} = 0$ to be

$$J_{heat,opt} = \Delta J_{in}/4 \tag{31}$$

with the maximum value of extractable power $P_{ex,max}$ to be:

$$P_{ex,max} = \frac{\Delta J_{in}}{4} \cdot \frac{T_h - T_c}{T_h} = \frac{\Delta J_{in}}{8} \cdot \frac{T_{h,0} - T_{c,0}}{T_{h,0}}$$
(32)

where $T_{h,0}$ and $T_{c,0}$ are the respective radiative equilibrium temperatures, i.e. in the absence of heat transport $(J_{heat} = 0)$. We note that the extracted power is only a quarter of the power associated with the Carnot efficiency (Eq. (28)). If we furthermore consider that $\Delta T (J_{ex} = 0) = 2 \cdot \Delta T (J_{ex,max})$, the overall power that can be extracted is reduced further to merely $\approx 13\%$ of the power of the system that would be predicted using the Carnot efficiency and the radiative equilibrium temperatures. If we use the concrete numbers of the model, we obtain as an overall maximum efficiency $\eta_{max} = P_{ex,max}/\Delta J_{in} = 1/8 \cdot (45/288) \approx 2\%$, which corresponds closely with the actual reported efficiency of the atmospheric circulation [46]. This maximum as well as related sensitivities of the model variables are shown in Fig. 7.

We can relate this maximum in power extraction to the more general principle, the proposed principle of Maximum Entropy Production (MEP) [23–25,27]. We note that in the above equations, for small temperature differences, maximizing power extraction and dissipation is almost equivalent to maximizing entropy production. This can easily be shown by using σ_{heat} rather than P_{ex} . Then, we get, using equivalent terms:

$$\sigma_{ex} = J_{heat} \cdot \frac{(\Delta J_{in} - 2J_{heat})}{k_d \cdot T_h T_c}$$
(33)

If, again, we neglect the dependency of T_h on J_{heat} in the denominator, we obtain:

$$J_{ex,max} \approx \Delta J_{in}/4, \qquad \sigma_{ex,max} \approx \Delta J_{in}^2/(8k_d \cdot T_h T_c) = P_{ex,max}/T_c \tag{34}$$

so that both, maximum extraction of power and MEP are associated with approximately the same optimum flux and for conditions at the Earth's surface are hard to distinguish. This close correspondence can also be seen in Fig. 7c.



Fig. 7. Sensitivity of the steady state of the model of Section 2.3 to the heat exchange flux J_{heat} between the boxes. Shown are: (a) temperatures; (b) entropies of the two boxes S_h and S_c as well as the total entropy of the system S_{tot} ; (c) extracted power P_{ex} and entropy production σ_{heat} by the heat exchange between the two boxes; and (d) Helmholtz free energy A and disequilibrium entropy S_{diseq} .

4.5. Using power to drive disequilibrium in the momentum balance

I now consider the case in which the extracted power from the temperature gradient is used to drive large-scale motion, that is, the power is used to create a gradient in the momentum balance. To formulate the momentum balance, I use again a two-box representation, characterized by two velocities v_h and v_l that form the gradient in momentum (see Fig. 8a). The imported power into the system P_{in} results in a force F_{acc} that accelerates v_h at the same time as the counterforce acts on v_l in the opposite direction. Hence, the accelerating force results in the creation of a momentum gradient. The power that is put into this flow is given by $P_{in} = F_{acc} \cdot (v_h - v_l)$. We write the momentum balances for the two boxes as:

$$\frac{d(\rho_h \cdot v_h)}{dt} = F_{acc} - J_{mom}, \qquad \frac{d(\rho_l \cdot v_l)}{dt} = J_{mom} - F_{acc}$$
(35)

Here, F_{acc} is the accelerating force resulting from the input of power, and J_{mom} is the momentum flux that depletes the gradient in momentum (i.e. a friction force). This momentum flux is written as $J_{mom} = k_{mom} \cdot (v_h - v_l)$, where k_{mom} is a momentum "diffusion" parameter that characterizes friction.

I express the free energy A_{mom} associated with motion and the disequilibrium entropy S_{mom} that is associated with the momentum gradient in terms of the reduction in entropy due to the import of power and due to the dissipation of the momentum gradient by J_{mom} , as in Eqs. (17) and (18):

$$\frac{dA_{mom}}{dt} = P_{in} - D_{mom} \tag{36}$$

and

$$\frac{dS_{mom}}{dt} = -\frac{P_{in}}{T} + \frac{D_{mom}}{T} = -\frac{P_{in}}{T} + \sigma_{mom}$$
(37)

where D_{mom} is the dissipation of the momentum gradient, written as $D_{mom} = J_{mom} \cdot (v_h - v_l)$, and σ_{mom} is the entropy produced by frictional dissipation, with $\sigma_{mom} = D_{mom}/T$. The analytical solutions of these equations are given in

V_h

i 00

100 * v

80



power, dissipation Free Energy A_{mom} (10⁶ J m⁻²) (W m⁻²) mom (103 1 َ ≊m 즛 0 Ò 10 20 30 40 50 20 30 Ó 10 40 50 Time Time

Fig. 8. A simple model to illustrate the formation of a gradient in momentum and a resulting evolutionary trend away from thermodynamic equilibrium due to work performed on the system. (a) Setup of the model; (b) velocities v_h and v_l ; (c) import of power P_{in} and frictional dissipation D_{mom}; (d) free energy A_{mom} and disequilibrium entropy S_{mom}. The plots were computed with the model developed in the text and values of $\rho_h = \rho_{air} \approx 1 \text{ kg m}^{-3}$, $\rho_l = \rho_{water} \approx 1000 \text{ kg m}^{-3}$, $P_{in} = 2 \text{ W m}^{-2}$, and $\tau_{mom} = 7 \text{ d}$. To compute the velocities, an average height of a boundary layer of 1000 m has been assumed.

Appendix A, where it is also shown that the resulting free energy A_{mom} in steady state is identical to the well-known expression for the kinetic energy associated with motion.

An example of the temporal evolution from rest to a steady state in which a momentum gradient is maintained is shown in Fig. 8. While constant power is put into the system, resulting in a net acceleration and the build-up of the velocities (Fig. 8b), dissipation catches up with power input as velocities increase (Fig. 8c). In steady state, the dissipation balances the input of power, the resulting free energy in form of kinetic energy reaches a steady state value, as does the associated entropy (Fig. 8d).

This sensitivity of the model to P_{in} is shown in Fig. 9. We find that the extent of thermodynamic disequilibrium reflects the combination of power input as well as the intensity of dissipation (as formulated in more general terms in Eq. (22)). Since dissipation in the model always lags after the power imported into the system, higher power import results in states further away from thermodynamic equilibrium. The "efficiency" by which the momentum gradient is dissipated, as reflected in the value of k_{mom} , also plays an important role. Greater values of k_{mom} deplete the gradient faster, and hence result in a steady state closer to thermodynamic equilibrium (also shown in Fig. 9).

While this example is clearly highly simplistic, it nevertheless demonstrates the following important points: First it shows how the input of power results in the generation of free energy in the form of kinetic energy. Second, it shows how the resulting free energy in steady state reflects the past net work done on the system. And thirdly, it shows how the extent of disequilibrium is directly related to the magnitude of power input and the intensity of dissipation.

4.6. Transferring maximum power to motion

The momentum balance model included a constant input of power, an assumption that we can now relax by (a) using the dependence of extractable power P_{ex} on the heat flux J_{heat} from the heat balance model (Eq. (30)) and by (b) linking the resulting motion to the transport of heat, i.e. to the heat flux J_{heat} . This transport of heat in the Earth's



Fig. 9. Sensitivity of thermodynamic disequilibrium, as measured by $S_{max} - S$, to the import of power P_{in} and the "efficiency" by which it is dissipated, which is reflected in the value of k_{mom} in the model. The three lines correspond to values of $k_{mom} = 0.002 \text{ kg m s}^{-1}$ (dotted line), $k_{mom} = 0.02 \text{ kg m s}^{-1}$ (solid line), and $k_{mom} = 0.2 \text{ kg m s}^{-1}$ (dotted line).

atmosphere is not accomplished by the mean flow, but much more so by the turbulent exchange processes between the surface and the atmospheric boundary layer and by the baroclinic activity in the mid latitudes for the exchange of heat between the tropics and the poles. The heat flux J_{heat} is therefore expressed to be proportional to the turbulent exchange of momentum – as expressed by k_{mom} – and the temperature gradient ΔT (as done in common parameterizations of turbulent heat fluxes at the surface), neglecting the contribution from latent heat for simplicity:

$$J_{heat} = k_{mom} \cdot c_p \Delta T \tag{38}$$

Since $\Delta T = (\Delta J_{in} - 2J_{heat})/k_b$, this yields the dependence of J_{heat} on k_{mom} of

$$J_{heat} = \frac{k_{mom}c_p}{2k_{mom}c_p + k_b} \cdot \Delta J_{in} \tag{39}$$

This reformulation of J_{heat} does not alter the dependence of P_{ex} on J_{heat} and the associated optimum value of the heat flux that maximizes the extraction of power. Rather, the optimum friction coefficient $k_{mom,opt}$ that results in maximum power in the flow is given by equating (31) with (39):

$$k_{mom,opt} = \frac{k_b}{2c_p} \tag{40}$$

The resulting free energy $A_{mom,opt}$ at maximum power is then given by:

$$A_{mom,opt} = \rho_e \cdot \frac{c_p}{k_b} \cdot P_{ex,max} \tag{41}$$

What this example shows us is that maximum power can be extracted from the radiative gradient and converted into motion if friction has the "freedom" to adjust to such an optimum value. While the maximum value of extracted power only depends on radiative properties, but not on the characteristics of the fluid (cf. Eq. (32)), the resulting motion and disequilibrium, as represented by $A_{mom,opt}$ and $S_{mom,opt}$ depend on fluid properties such as density and heat capacity as well as radiative properties of the atmosphere (as represented by k_b). The fact that the present-day energetics of the Earth's atmosphere in terms of its thermodynamic efficiency is consistent with maximum power generation, we could argue that the way that momentum is generated and dissipated would arrange itself in such a way as to maximize the extraction of power from the radiative gradient. This maximization, however, requires flexible boundary conditions in the planetary energy balance that allows for enhanced entropy export at the planetary scale in the presence of motion that redistributes heat.

4.7. Using motion to perform work

The free energy associated with motion can be used to perform further work, but, again, thermodynamics sets the limits on the maximum possible rate at which power can be extracted from the flow. To show this, I develop another simple box model to establish a first-order simple estimate of maximum power transfer from flow. We consider a volume of moving fluid or air with an underlying solid material (see Fig. 10). This volume V is defined by a height



Fig. 10. Simple model to illustrate maximum power from motion. (a) Model setup; (b) sensitivity of the power involved in lifting, P_l and export of kinetic energy of the fluid P_o and the solid mass P_m to the export velocity v_o . The plots were computed with the model developed in the text and values of $\rho_i = 1 \text{ kg/m}^3$, $v_i = 1 \text{ m/s}$, H = 10 m, $g = 9.81 \text{ m/s}^2$ and $A = 200 \text{ m}^2$.

H, length *L*, and a fixed cross section to the flow of $A = H \cdot B$. The inflow is characterized by a velocity v_i with a density ρ_i , and the outflow by a velocity v_o and respective density ρ_o of the fluid. Power is transferred from the inflow to lift mass at a rate J_m , which is exported in suspension at velocity v_o and a density of ρ_m .

The fluid and solid transports are constrained by mass conservation in steady state by:

$$\rho_i \cdot v_i = \rho_o \cdot v_o \tag{42}$$

and

$$J_m = \rho_m \cdot A \cdot v_o \tag{43}$$

Furthermore, the dynamics of the transfer process is constrained by the work balance, which balances the inflow of kinetic energy P_i with the work done to lift and accelerate solid mass P_m and the export of kinetic energy P_o :

$$P_i = P_o + P_m \tag{44}$$

The flow rates P_i and P_o are given by:

$$P_i = \frac{\rho_i}{2} \cdot A \cdot v_i^3, \qquad P_o = \frac{\rho_o}{2} \cdot A \cdot v_o^3 \tag{45}$$

The power P_m needed to lift and accelerate mass result in two terms, the work P_l to continuously lift mass at a rate J_m to a mean height of H/2:

$$P_l = J_m \cdot g \cdot H/2 \tag{46}$$

and the work P_t to accelerate the mass to the export velocity v_o :

$$P_t = J_m \cdot \frac{v_o^2}{2} = \frac{\rho_m}{2} \cdot A \cdot v_o^3 \tag{47}$$

We calculate the maximum power transferable into solid mass transport by maximizing P_t with respect to v_o . To do so, we express J_m as a function of v_o using Eq. (44):

$$J_m = \frac{A}{gH} \left(\rho_i v_i^3 - (\rho_o + \rho_m) v_o^3 \right) \tag{48}$$

We express ρ_o as a function of v_o using Eq. (42) and ρ_m as a function of J_m and v_o using Eq. (43) to get:

$$J_m = J_i \cdot \frac{v_i^2 - v_o^2}{gH + v_o^2}$$
(49)

simplified by expressing the influx of mass as $J_i = \rho_i v_i A$. This yields a dependency of the power involved in mass transport P_t of

$$P_t(v_o) = J_i \cdot \frac{v_i^2 - v_o^2}{gH + v_o^2} \cdot \frac{v_o^2}{2}$$
(50)

Table 2			

Four sources (A	, В,	C, D) f	for powering	Earth system	processes and	d their magnitude.
-----------------	------	---------	--------------	--------------	---------------	--------------------

	Source of power	Magnitude (TW)
A	Solar radiation (total)	166 000
	Difference in photon composition	41 000
	Vertical heating gradient	83 000
	Spatial insolation gradient	46 000
	Temporal insolation gradient	170
В	Initial conditions of inner Earth (total)	< 50
	Secular cooling	33
	Radioactive decay	17
С	Angular momentum (total)	5
	Depletion of Moon's gravitational field	3.5
	Depletion of Sun's gravitational field	1.5
D	Cosmic radiation	?

To get a simple approximation for the maximum power of $P_{t,max}$, I assume that $gH + v_o^2 \approx gH + v_i^2$, to get the optimum flux $J_{m,opti}$ of:

$$J_{m,opti} = \frac{1}{2} \cdot \frac{P_i}{gH + v_i^2} \tag{51}$$

and the maximum transferable power $P_{t,max}$ of:

$$P_{t,max} = \frac{1}{2} \cdot \frac{v_i^2}{gH + v_i^2} \cdot P_i \tag{52}$$

What Eq. (52) tells us is that at best about half of the imported, kinetic energy of the flow can be transferred to perform work. If we were to include inevitable frictional losses as well, this efficiency would decline to maximum efficiencies much lower than a half.

4.8. Components for a hierarchy of power transfer

The models developed in Sections 4.4–4.7 are building blocks that provide the basis to understand power transfer within a hierarchy of Earth system processes as shown in Fig. 1. The general reduction of power to much less than the Carnot efficiency should be seen as a general feature of Earth system processes since in this complex system many processes compete for dissipating free energy. In concrete terms, the simple models developed here show that power transfer from solar radiation to motion to other forms of power (e.g. geochemical cycling) by abiotic means is limited by very low efficiencies, so that potentially little power is available in the end for driving disequilibrium and geochemical cycling. What is needed next is to assess how much power is potentially available in the first place before we estimate how much of this power is transferred by Earth system processes to geochemical cycling and what the role of life is in generating chemical free energy.

5. Drivers of the thermodynamic machinery of planet Earth

To understand the limits of how much free energy can be generated, we now look at the potential external sources that can be used to power Earth system processes. There are four primary sources of power for Earth system processes: (A) solar radiation, (B) depletion of initial conditions of the interior Earth, (C) depletion of the angular momentum of celestial bodies, and (D) cosmic radiation. These sources, the associated power and types of free energy generated is summarized in Table 2.

5.1. Solar radiation

The most dominant source that can be used to derive power is the influx of solar radiation. There are different forms of power that can be derived from this flux. While all of it can in principle be used by absorption to produce heat and thereby create gradients in temperature, some parts of it can be used to drive photochemistry. The narrow confinement of solar radiation to a relatively small solid angle can also be used to create free energy. In the following, the power that can be extracted to drive photochemistry and from gradients in heating is estimated.

To estimate the associated power with different aspects of solar radiation, we start with the gross influx at the top of the atmosphere. The present-day average value for this influx is about 342 W m⁻² [47], which by using the surface area of the Earth, $511 \cdot 10^{12}$ m², yields a global total sum of about 175 000 TW (1 TW = 10^{12} W). The maximum that could be converted into work is constrained by the efficiency given by the difference in radiative temperatures of the Sun ($T_{sun} \approx 5760$ K) and of Earth ($T_{earth} = 278$ K, corresponding to an absorption of 342 W m⁻²). Using the typical thermodynamic expressions yield a maximum efficiency of 95%, reducing the maximum work possible at the planetary scale to 166 000 TW. However, about 30% of this radiative flux is reflected, by the presence of clouds within the atmosphere and a reflective surface at the ground (e.g. ice cover), reducing the total to 116 000 TW.

This value of 116000 TW is a theoretical maximum because it would require using the difference in photon energy to extract this amount of power. This is for instance possible by performing photochemistry. However, only a certain range of wavelengths are suitable for photochemistry. The associated photons need to be energetic enough to at least excite electrons. To estimate the limit on the maximum power that could be used by photochemistry, we consider two different forms of absorption that generates chemical free energy. First, radiation with wavelengths λ shorter than visible light ($\lambda < 400$ nm) in the ultraviolet and above results in photodissociation and ionization [47]. Assuming a blackbody distribution of solar radiation, this radiation is about 10% of the 116000 TW, yielding about 12 000 TW potentially available to perform work by dissociation and ionization. While this can result in some chemistry, most notably stratospheric ozone production, its high energetic nature tends to destroy molecules rather than to drive chemistry that builds more complex molecules. Hence, this fraction of the solar spectrum is excluded here from the considerations as it is unlikely to yield chemical free energy usable for longer-lasting low entropy states. Radiation in the visible band (400 nm $< \lambda < 700$ nm), in contrast, is absorbed mostly by electronic absorption, which then can result in photochemistry, such as photosynthesis, which can then convert the photon energy into chemical free energy. This fraction is about 35% of the solar spectrum, and corresponds to about 41000 TW. Radiation with wavelengths longer than in the visible range (infrared and longer, $\lambda > 700$ nm) is absorbed mostly by rotational and vibrational modes, which is associated solely with the generation of heat.

Most of the absorption of solar radiation takes place at the surface, while the planet is cooled mostly by the emission of radiation from greenhouse gases in the atmosphere aloft. In the global mean, about 50% of the incident solar radiation is absorbed at the surface, resulting in radiative heating. Using the numbers from above, this results in maximum theoretical work of about 83 000 TW. However, extracting work from this gradient competes with the radiative exchange, which also depletes this gradient, so a maximum power exists that can be extracted from this driver [48–51,37]. Following the same line of reasoning as in the last section, the simple model of Appendix B results in about 1/2 of the heat flux being able to be extracted to perform work at a maximum efficiency of 11.4%, yielding about 5000 TW.

A similar radiative gradient exists due to the geometry of the Earth, in which surfaces are not heated evenly by solar radiation. In the tropics, the incident radiation is more normal to the surface, hence receive a higher flux of solar radiation per unit area than the poles. For the same incident flux, the tropics receive about 20% more solar radiation than the global mean (averaged over half of the planetary surface from 30° S to 30° N), while the extratropics receive about 80% of the global mean. Hence, the magnitude of this mean spatial forcing is in the order of 46 000 TW. This zonal gradient of radiative heating is used within the Earth system to drive the large-scale atmospheric circulation, similar to the example shown in Section 4.4. As shown in Section 4.4, the maximum efficiency by which this forcing can be converted into power is rather small with 2%, yielding a power of merely 900 TW to drive the generation of kinetic energy.

Temporally varying heating of the surface can be used to extract work e.g. for the physical weathering of rocks (see Appendix C). Since it depends on local material properties and strongly on the magnitude of temperature variations, it is difficult to put a global, maximum value on this aspect. Simulations with a land surface model (Fabian Gans, pers. comm.) yield a value of about 50 TW (global land). Using a land fraction of about 30% we can scale this number to

yield a global estimate in the order of 170 TW. This number is used here merely to place an order of magnitude on this source and does not necessarily represent the maximum possible power extractable from temporal variations.

What is not included here is the power that can be extracted from the small solid angle of direct solar radiation. The small solid angle of direct solar radiation could be used to focus the incoming radiation to a smaller area, thereby driving a heat engine with a high temperature gradient. While this aspect could be used as a means to generate power (e.g. "direct concentrated solar" power), it is not used by natural processes to derive power and is therefore not considered further.

5.2. Earth's interior

Fossil heat left over from the formation of the Earth 4.5 billion years ago as well as radiogenic heating by the decay of radionuclides result in temperature gradients within the solid Earth. These gradients are depleted by radiative and conductive processes, but also by the slow creeping motion of the mantle and the crust. With an average ground heat flux of less than 0.1 W m⁻², this yields a maximum power source of less than 50 TW. About 2/3 of this heat flux is attributed to the secular cooling of the interior, mostly in form of the crystallization of the core.

Due to the competition of work extraction from this heating gradient with radiative-conductive processes, a maximum power that can be used to material cycling has been shown to exist [52–54]. Similar to the simple model of the vertical gradient within the atmosphere Appendix B yields that a maximum of about 1/2 of the potential, i.e. 25 TW, can be converted into power to drive motion.

5.3. Celestial bodies

Power associated with the angular momentum of other celestial bodies can be extracted to generate potential energy in form of tides on Earth [55]. The power input into the Earth system is in the order of 5 TW, and is mostly derived from the Moon (3.5 TW) and the Sun (1.5 TW).

5.4. Cosmic radiation

In principle, work could be extracted from cosmic radiation, the flux of gamma rays and highly energetic particles from space to the Earth's atmosphere. However, this flux would seem to provide merely a small amount of power, and, since it is highly energetic, it is likely to destroy complex molecules, rather than creating longer lasting free energy. Hence, this potential source is not considered further.

6. Hierarchy of power transfer within the Earth system

We now have the necessary components to build a hierarchical view of power transfer of planet Earth and how it is altered by life in quantitative terms. I first describe this hierarchy of power transfer qualitatively before I discuss life in the context of where it gets its power from this hierarchy to sustain itself and how it alters the power generation of the planet. The strength of the different processes of this hierarchy – including life – is then summarized in an estimate of the global work budget. Then, several examples are given to show that the assumption of maximized generation, dissipation, or transfer of power within this hierarchy yields realistic descriptions of the strength of processes within the hierarchy as well as for life. The application of maximized power generation at the planetary scale and associated states of disequilibrium are then related to the Gaia hypothesis at the end of this section.

6.1. A hierarchy of power transfer

The two largest sources for power generation for surface and interior processes – absorption of solar radiation and heat in the interior – are the natural starting points for a planetary hierarchy of power generation and transfer. This hierarchy is summarized in Fig. 11. It is necessarily simplified and excludes many processes, but is used here to (a) illustrate the importance of the hierarchical view in understanding power generation and transfer, (b) place interactions among Earth system processes in the context of power transfer, and (c) describe power transfer for the most important processes that drive geochemical cycles and directly relate to life.



Fig. 11. Simplified summary of a hierarchy of power transfer among Earth system processes. Solid arrows describe flows of power, while dotted arrows describe effects. Based on [57] and [54].

6.1.1. Power transfer from solar radiation to atmosphere and surface

The primary driving force for generating power at the surface and above is the absorption of solar radiation and the associated gradients in radiative forcing. Differential heating causes temperature and density gradients that yield buoyancy forces. These forces fuel the generation of motion in the atmosphere, which then drives the cycling of water. When air is lifted, unsaturated air eventually reaches saturation, condenses, and precipitates, thereby effectively removing moisture from the atmosphere. The atmospheric circulation hence acts as a dehumidifier [19,20,56]. Dehumidification of the atmosphere also allows for the evaporation of sea water, which in addition to the phase change from liquid to gaseous also performs work in desalinating sea water. The strength of the dehumidifier and desalinator should to first order be directly related to the strength of updrafts, and hence to the strength of the large-scale atmospheric circulation.

The precipitation of atmospheric vapor on land provides the basis to chemically dissolve rock minerals – since the sea water was desalinated upon evaporation – and to transport sediments in suspension in river flow. This then provides the power to transform and transport rock minerals on land, which is the basis for strong geochemical cycling at the surface. The strength of this cycling should to first order depend on the strength of the hydrologic cycle.

This line of abiotic forms of power transfer from radiative gradients to temperature gradients to motion to hydrologic cycling to geochemical cycling at the surface is indicated by the solid arrows in Fig. 11. Each of these steps is associated with important, first-order effects that alter the ability to generate power within the hierarchy (dotted arrows in Fig. 11). Motion transports sensible and latent heat, thereby depleting the temperature gradients that fuels the motion. Hydrologic and geochemical cycling affect the composition of the atmosphere, particularly regarding the concentration of water vapor, clouds, and other important factors that affect radiative exchange within the atmosphere. These in turn affect radiative gradients that are the indirect driving forces for hydrologic and geochemical cycling. Hence, we have strong coupling and resulting interactions between the power transferred into a process within the hierarchy and the effects that this process has on the power source.

6.1.2. Power transfer from internal heating to mantle and surface

Similar layers of power generation, transfer and effects can be formulated for Earth's interior processes (shown in the lower half of Fig. 11, following Dyke et al. [54]). Here, the primary source for power is the secular cooling of the interior, mostly by the crystallization of the core, and heating by radioactive decay within the crust. The resulting differential heating results in buoyancy forces – just like within the atmosphere – that powers the slow, creeping motion of the mantle. The strength of mantle convection should be directly proportional to the strength of heating. In the upper part of the convecting mantle, the asthenosphere, the hot material of the mantle is lighter than the cooled oceanic crust at the surface–interior boundary. The resulting buoyancy forces result in the cycling of oceanic crust, with new oceanic crust forming at mid-oceanic ridges, seafloor spreading, and subsequent subduction of cooled oceanic crust. The power to drive oceanic crust cycling comes from the differential heating from the mantle below, and the surface–atmosphere above. Again, it is reasonable to assume that, to first order, the strength of oceanic crust cycling is directly associated with the strength of mantle convection.

Mostly within the subduction zones of the oceanic crust, the melting of the crust allows the separation of lighter compounds from the heavier basaltic crust which then produces the material to form continental rocks. With higher rates of subduction, it would seem reasonable to assume that this yields higher rates of continental rock formulation and tectonic uplift of continental crust. The cycling of continental crust is then closed by the chemical weathering of rocks and the material transport on land. The power to lift continental crust comes from the subduction of oceanic crust. Hence, the rate of continental crust cycling should be driven, to first order, by the rates of subduction and oceanic crust cycling in general.

The transfer of power from the source of differential heating in the interior to mantle convection to oceanic and continental crust cycling are again indicated by the solid arrows in Fig. 11. Again, each of these steps is associated with important, first order effects that alter the ability to generate power within the hierarchy. These effects are shown by the dotted arrows in Fig. 11. Mantle convection transports heat, as does oceanic crust cycling, thereby depleting the temperature gradient that drives the motion. The extent and thickness of continental crust alters heat transport by essentially acting as an insulator "floating" on the upper mantle [58]. Geochemical cycling alters the properties of the oceanic crust, e.g. by hydration, thereby affecting the conditions under which oceanic crust melts. As in the case above of the hierarchy driven by solar radiation, we have strong coupling and interactions within the hierarchy of power transfer within the Earth's interior from the interior power source to surface processes as well.

6.1.3. Aspects omitted from the hierarchy

Of course, the hierarchy described here is highly simplified and other processes that generate or transfer power are not shown. These would lead to similar hierarchies, so the hierarchy shown in Fig. 11 is necessarily incomplete.

For instance, one power source described in Section 5 is in the form of temporal variations in radiative heating. The resulting varying heating and cooling of air could also result in dehumidification of air. However, it would seem that this is a rather local effect that is unlikely to contribute substantially to large-scale cycling of water. Also, heating and cooling of the surface can be utilized to perform the physical work to break rocks (physical weathering), which increases the surface area available for chemical weathering, thereby possibly enhancing the efficiency of chemical weathering. Hence, temporal variations as a power source would likely lead to another hierarchy of power transfer that would interact with the one shown in Fig. 11.

What has not been described within the hierarchy are processes that are also driven by atmospheric motion. For instance, the atmospheric electric circuit [59] is linked to the strength of tropical convection, specifically to the associated charge separation in thunderstorm clouds. The power needed to separate charges is taken from the power contained in convecting motion. Hence, the strength of the atmospheric electric circuit should relate to the strength of the atmospheric circuit should relate to the strength of the atmospheric circuit should relate is not entirely dissipated

by turbulence. Rather, some momentum is transferred to the transport of liquids and solids at the surface. Over the ocean, power is removed from the atmosphere to generate ocean waves and transferred further to drive the winddriven circulation [22]. Over land, power is removed to transport dust and drive mass transport that creates dunes [60]. Hence, the hierarchy shown in Fig. 11 is merely an incomplete, first attempt to arrange Earth system processes into a hierarchy of power transfer.

6.2. Coupling of atmosphere-surface-interior processes and life

The hierarchies driven by solar radiation and interior heat intersect at the surface, where both drivers indirectly affect the strength of geochemical cycling. The power supplied by the hierarchies from either side can limit the rates of geochemical cycling, either by limiting the supply of fresh rock material by uplift or outgassing from below, or by the transformations and transport that are driven by atmospheric processes, such as the material transport on land is driven by precipitation. Since this availability of power for geochemical processes at the surface is directly linked to the extent of thermodynamic disequilibrium – for instance in terms of atmospheric composition or in terms of the redox gradient between the atmosphere and the Earth's crust – the power available at the surface plays a critical role for the thermodynamic state of the planet. And this is exactly where life comes in. The surface is where most of life is taking place, potentially adding much fuel to this limiting bottleneck in geochemical cycling. To understand the potential of biotic processes in adding extra power, we need to briefly elaborate on the different types of lifeforms and their effects.

Without going into the philosophical question of what life is [29], I focus here on viewing life as being relatively persistent, replicating structures that are maintained by a myriad of metabolic reactions that are driven by the depletion of chemical free energy. Depending on how the chemical free energy was generated, we distinguish autotrophic from heterotrophic life, and chemotrophic from phototrophic life. Autotrophic life uses sources of free energy from the environment, either in form of chemical compounds (chemoautotrophs) or by using light (photoautotrophs). Heterotrophic life requires organic carbon to grow, mostly produced by other organisms, as a source of free energy.

The consequences of these different types on power generation is rather different. Chemotrophic life depletes sources of chemical free energy generated by abiotic processes. This generation of chemical free energy should be directly related to, and drawn from the power involved in the physical processes within the hierarchies shown in Fig. 11. Hence, it is unlikely that it adds to the power generation ability within the planetary hierarchy, but rather accelerates the transformations of the associated geochemical compounds to a state of thermodynamic equilibrium. The same holds for heterotrophic life, which depletes free energy stored in organic compounds. Phototrophic life, in contrast, has a very different effect. By utilizing the parts of the solar spectrum able to drive photochemistry, phototrophic life generates additional chemical free energy and "skips" the limitations and inefficiencies associated with the physical transformations of power from sunlight to geochemical power. Hence, phototrophic life is in principle able to contribute substantial power to geochemical cycling.

The power generated by photosynthesis is used to maintain and grow the photosynthesizing organisms, resulting in autotrophic respiration. The free energy contained in litter, detritus as well as grazing feeds heterotrophs and associated food webs. In order to build biomass, sunlight needs to be absorbed and nutrients need to be drawn from the environment (solid arrows in Fig. 11). By doing so, life alters unavoidably the light absorbing characteristics of the surface as well as the geochemical environment (dashed arrows in Fig. 11). Just as discussed above in the examples of abiotic processes, we would expect that overall stronger photosynthetic activity would result in higher rates of alterations in the geochemical environment.

6.3. The global work budget

The power involved in the different processes within the hierarchy are quantified by the global work budget. The following estimates are first-order, rough approximations for present-day conditions, and are summarized in Table 3.

At the top of the hierarchy, differential radiative heating fuels atmospheric motion. A well established number for the power for generating kinetic energy associated with the large-scale atmospheric circulation is about 900 TW [46] although there is some uncertainty in this number and a recent estimate places this number at 1052–1298 TW [61]. Not all of this power is dissipated in the atmosphere, but some of it is transferred to perform other work. For instance,

Process	Magnitude	Type of free
	(TW)	energy generated
Atmosphere–surface processes		
Atmospheric motion	900	Kinetic energy
Oceanic motion	1	Kinetic energy
Hydrologic cycling	558	Potential energy
Desalination	27	Chemical energy
Continental runoff	13	Kinetic energy
Dissolution on land	< 1	Chemical energy
Interior–surface processes		
Mantle convection	12	Kinetic energy
Oceanic crust cycling	28	Kinetic energy
Continental crust cycling	< 1	Potential energy
Biospheric processes		
Terrestrial productivity	152	Chemical energy
Marine productivity	63	Chemical energy
Anthropospheric processes		
Human appropriation of productivity	30	Chemical energy
Primary energy consumption	17	Chemical energy

Table 3 An estimate of the global work budget of planet Earth. See text for derivations and references.

65 TW of power is transferred into generation of ocean waves at the sea surface, of which about 1 TW is transferred to drive the wind-driven ocean circulation [22].

The work done by hydrologic cycling consists of several terms, including the work of lifting, expansion, compression, desalination, etc. [19,20]. The work done by lifting the amount of annual rainfall to the level at which condensation occurs corresponds to about 558 TW. This number is derived from model simulations of an Earth system model of intermediate complexity [62] in which the work of lifting was diagnosed (unpublished results by the author). This work corresponds to lifting the annual amount of precipitation of about $423 \cdot 10^{12} \text{ m}^3 \text{ yr}^{-1}$ [46] to a height of about 4200 m. Peak values are found in the tropics of about 4 W m⁻², which is consistent with numbers estimated previously [63].

Work is also performed to desalinate seawater upon evaporation from the ocean surface. This power can be estimated by using the total flux of ocean evaporation of $361 \cdot 10^{12} \text{ m}^3/\text{yr}$ [46] and the work that sea salt could perform upon mixing with freshwater [64]. Using a mean sea salt concentration of 35.153 g/kg [65], a mean molar weight of 70.629 g/mol, and an assumed van't Hoff factor of 2, this yields a power source of 27 TW generated by the evaporation of seawater from the world's oceans. Note that this work is not derived from the hierarchy of power transfer, but is contained in the value of latent heat of vaporization of sea water. Nevertheless, it is indirectly related to the strength of dehumidification of the atmosphere since unsaturated air is needed to drive surface evaporation. The other forms of work associated with hydrologic cycling, in particular compression and expansion of water vapor during evaporation and condensation, is not explored further here because this work is not transferred within the hierarchy. The reader is referred to other studies for details on these aspects [19,20].

When precipitation occurs on land, most of its potential energy is dissipated by frictional dissipation, but some potential energy is regained because the elevation of land is mostly above sea level. The rate at which this potential energy is generated is about 13 TW and was estimated from a simulation with a global land surface model in conjunction with present-day climatological forcing and topography (unpublished results by the author).

The desalinated water derived from precipitation on land is able to perform chemical work by dissolving rock-based minerals. Most of the rock minerals on land are not sodium chloride, so only a fraction of the work contained in the estimate of desalination can be used. Assuming that ocean water is in equilibrium with the composition of the crust, this work is estimated by combining the estimated value of continental runoff of $33 \cdot 10^{12} \text{ m}^3 \text{ yr}^{-1}$ [46] (which in the mean equals the net moisture transport to land by the atmospheric circulation) with the above estimate of desalination, reduced by the fraction of salts other than sodium chloride in the total salt concentration of sea water of about 6%. This yields an estimate for the work by dissolution of minerals on land of $33/361 \cdot 6\% \cdot 27 \text{ TW} = 0.15 \text{ TW}$.

The values for interior processes (mantle convection, oceanic and continental crust cycling) are derived from simple models assuming maximum power for mantle convection, oceanic crust cycling and continental uplift [54]. While these numbers are highly uncertain, the sum of them are constrained by a total heat flux from the interior of about 50 TW but are reduced due to the general thermodynamic inefficiencies discussed above.

The power contained in biotic activity is derived from the gross rates of carbon assimilation and assuming that the assimilated carbon compounds contain a free energy similar to the one of sugar (479 kJ/mol). These numbers yield a generation rate of chemical free energy of 152 TW and 63 TW by photosynthesis on land and ocean respectively [26,54].

For completeness and for the discussion section below, human energy consumption is also listed in Table 3. Humans primarily use two forms of energy – they appropriate productivity of the biosphere for their use (particularly to meet metabolic energy demands), most dominantly in form of agriculture. It is estimated that in the order of 40% of the terrestrial net primary productivity is appropriated for human use [66–68]. Noting that net primary productivity is typically about 50% of gross photosynthesis, this yields a number of about $0.4 \cdot 0.5 \cdot 152$ TW = 30 TW. Humans also use primary energy for industrial use, transport, mostly from fossil resources. Assuming that all of the primary energy consumption is based on non-renewable resources, this adds another 17 TW to human energy consumption [69].

A brief inspection of the magnitudes of power involved in different Earth system processes shown in Table 3 already emphasizes that life contributes substantially to the generation of chemical free energy to the planetary budget. This is particularly the case for material transformations on land: While abiotic processes (runoff, dissolution, continental crust cycling) potentially involve less than 15 TW, terrestrial productivity involves an order of magnitude more geochemical power. At the same time, we also note that human activity is a substantial geologic force. With a combined dissipation of about 47 TW, it is greater than all geologic processes (≈ 41 TW) within the Earth system.

A word of caution is appropriate here. Table 3 does not show that some of the processes listed are transferred from other processes. For instance, some of the power contained in hydrologic cycling should reflect power transferred from the atmospheric circulation. Likewise, human appropriation of terrestrial productivity transfers power from biotic activity. Hence, one would need to account for the interdependencies of these numbers in a more refined version of this budget.

6.4. Maximizing power generation and transfer

There are several studies that indicate that power generation and transfer is maximized for Earth system processes. That is, that the numbers shown in Table 3 are the maximum possible rates of power generation.

To start, the generation rate for atmospheric motion is close to the power that can be extracted from large-scale heating gradient to fuel motion (cf. Section 4), suggesting that the Earth's atmospheric circulation operates at its maximum strength. This was initially suggested by Edward Lorenz [70], and is closely related to the hypothesis formulated by Paltridge [71,13,72] that the atmospheric circulation maximizes entropy production. Since then, further work has shown that MEP yields reasonable predictions of hemispheric heat transport on other planetary bodies [14,73] and of empirical friction coefficients in atmospheric general circulation models [15,74], but also for vertical convection [71,75,49,37,51,76] and convection at hydrothermal vents at the seafloor [77]. More support comes from studies of turbulence and its effects on heat transport and entropy production [78–82].

For hydrologic cycling, Pauluis and Held [19,20,56] derived an entropy budget of the hydrologic cycle and the effect of hydrologic cycle on convection using the assumption of maximum work. Even though their work does not express power generation and transformation as is done here, it would seem that their analysis could easily be expressed in terms of hierarchical power transfer, but this aspect would need to be explored further. Once water is on land, several exploratory research papers investigated the use of thermodynamic maximization principles for soil processes and the partitioning of hydrologic fluxes at the land surface [83–87]. For river flow, a body of research suggests that river basins are organized to minimize energy expenditure of the river flow [88–90] and that this minimization is associated with characteristic power law scaling behavior of river basins [91,92]. While Rinaldo and Rodriguez-Iturbe's work [88–90] employed a minimization principle associated with energy dissipation of water flow, we can reinterpret their work here as a maximum transfer of power from river flow to sediment transport (as, e.g. demonstrated by the simple model in Section 4.7). For a given generation rate of kinetic energy associated with continental discharge, a maximum transfer of power from river flow to the work required to move sediment would translate into

minimum kinetic energy dissipation by river basins. Hence, their minimum energy expenditure assumption can be viewed as maximizing the transfer of power to sediment transport.

Maximizing sediment transport would affect the dynamics of continental mass as erosion depletes continental mass and acts to deplete the topographic gradient between land and ocean. In this context, Dyke et al. [54] showed with a simple model that an optimized erosion rate of continental mass exists that maximizes the work of uplift of continental mass. This maximum results from the trade-off of higher uplift rates with a higher erosion flux, but a lower erosion flux as a result of less topographic gradients. Their model showed that the maximization of continental crust cycling through sediment transport resulted in realistic values of the associated mean height of continental crust.

When looking at interior processes, there are a few studies that indicate that power generation (or entropy production) by mantle convection is maximized [52–54]. With a simple model similar to the two-box model of the atmosphere, Lorenz [53] showed that a state of Maximum Entropy Production associated with mantle convection yields interior temperatures that are consistent with those derived by conventional approaches. Dyke et al. [54] explored this line of reasoning further, showing that maximum generation and transfer rates exist from the generation of heating gradients by radioactive decay and secular cooling to mantle convection to the cycling of oceanic and continental crust. Although not fully explored, these studies nevertheless support the idea that maximum power generation, transfer and cycling by geologic processes seems to be a reasonable assumption.

When we now consider biotic activity, equivalent maximum power principles have been suggested for life [31–34]. Dewar [39] has recently related different optimality principles in plant physiology, such as maximum leaf photosynthesis and maximum growth in plant ecophysiology to the maximization of entropy production at different scales at which the system under consideration was defined. Since temperature was taken as a constant, Dewar's analysis is equally described by maximizing power generation by plant ecophysiological processes. At the ecosystem level, the maximization of entropy production was shown to be equivalent to the maximization of gross primary production, i.e. the gross carbon fixation by photosynthesis. This maximization was used in modelling studies to show that realistic rooting depths of vegetation [93–95] or function of leaf stomata (leaf openings that regulate water loss from the vegetation to the lower atmosphere) [96,97] can be derived that result in realistic values. In fact, using extreme climate model simulations of a "Desert World" and a "Green Planet" that yield the climatic conditions if all continents were bare or covered by rainforest [5], Kleidon [6] estimates that the effects of present-day terrestrial vegetation on climate yield environmental conditions that are close to maximizing terrestrial productivity.

These examples, however, are mostly seen in isolation. It is the interactions that would place these examples into the context of the planetary hierarchy. Nevertheless, these examples indicate that a whole range of natural Earth system processes may indeed be optimized, generating and transferring maximum rates of power through the planetary hierarchy.

6.5. Revisiting the Gaia hypothesis

With our understanding of how the Earth system generates power, how it transfers it, and how power is required to evolve thermodynamic variables away from equilibrium, we now revisit Lovelock's observation that the chemical disequilibrium within the Earth's atmosphere is a fundamental sign of widespread life. From the work budget shown in Table 3 we note that the generation of chemical energy by abiotic processes is rather limited. This power is needed for geochemical transformations, such as developing a redox gradient between the Earth's atmosphere and the crust. Dissolution of rocks on land is estimated to be less than 1 TW, while the generation of geochemical free energy by geologic processes, while not specified, must be considerably less than 40 TW, which is the upper limit to all power generated in the interior. Photosynthetic activity, in contrast, generates more than 200 TW of geochemical free energy, which is easily one to two orders of magnitude more than what abiotic processes can generate under present-day conditions. This simple estimation confirms Lovelock's qualitative observation that the chemical disequilibrium within the Earth's atmosphere is fueled mostly by the presence of widespread, photosynthetic life.

Out of this indication for widespread life on a planet, Lovelock later developed and proposed the Gaia hypothesis [40,41,30]. This hypothesis is associated with the common notions that life maintains the Earth in a homeostatic state, that conditions are optimal to life, and that the Earth system responds to change predominantly with negative, stabilizing feedbacks. This hypothesis has received widespread criticism but also led to highly innovative research [98,99].

We can understand the postulated implications of the Gaia hypothesis as the consequence of life's substantial generation of chemical free energy. Since life depends on environmental resources, particularly light, water and geochemical elements, the rate at which these are cycled strongly affects biotic activity and its ability to generate chemical free energy. The tendency of complex thermodynamic processes to maximize power generation would imply that environmental conditions are such that geochemical power generation by life is maximized. Since this involves vastly different time scales, with atmospheric turbulence taken place at time scales less than a day while the cycling of crust takes place at a time scale of millions of years, maximization of power generation cannot be achieved in an instant, but rather translate into a trend to increased power generation in time. Yet, when one process is maintained at maximum power generation, then the associated dynamics are necessarily stable and would react with negative feedbacks when perturbed.

With this in mind, we can reformulate the Gaia hypothesis on the basis of the requirement of chemical free energy generation to drive and maintain atmospheric chemical disequilibrium as follows:

Hypothesis: The Earth system has evolved further and further away from a state of thermodynamic equilibrium in time mostly by the increased generation rate of chemical free energy by life.

This hypothesis is well defined and can be evaluated quantitatively, but one would require a full understanding of the power generation and transfer processes within the Earth system and how these have changed in the past. Also, this formulation addresses the common objection to the Gaia hypothesis in that it assumes teleology [100,101]. The maximum power that can be transferred towards an inner layer of the onion depend only on the properties of an outer layer from which the power is extracted. For instance for the case of atmospheric heat transport, the maximum generation of kinetic energy is not a property of the fluid, but the maximum is entirely determined by radiative properties. This can be seen by inspecting the equation for maximum power from a radiative gradient (Eq. (32)), which does not depend on heat capacities, densities or friction constant. It is rather the conversion of this power to steady-state motion that is affected by material properties of the fluid (cf. Fig. 8). And the mere existence of a maximum power that can be extracted from an outer layer of the onion does not necessarily require the process of an inner layer to extract this maximum in power. Yet the indications cited above suggest, that the emergent, complex dynamics that are forced by such boundary conditions are organized in such a way that these indeed are close to maximum power extraction from an outer layer of the onion.

7. Discussion

The formulation of the hierarchy, the simple models and estimates of the previous sections clearly have their limitations and can be improved. Some of these are discussed in the following before some wider ranging implications of this thermodynamic view are discussed.

7.1. Limitations

There are certainly several limitations and aspects of the presented theory here and it should be only seen as a first sketch that needs improvement. The estimates of the global work budget can be improved by more detailed considerations, and the simple models to illustrate the hierarchy of power transfer can be fully coupled, and implemented in complex Earth system models to reproduce the postulated behavior. Also, not all power sources are included in the schematic diagram of Fig. 11 and other hierarchies exist in addition to the one shown, for instance regarding the transfer of power from atmospheric motion to the oceanic circulation.

Yet the fundamental importance of thermodynamic limits on power generation and transfer to understand disequilibrium and the emergent dynamics within the Earth system are unaffected by these relatively minor limitations. What is not entirely clear is which thermodynamic variable should be maximized. While the focus here is on maximizing power generation, this optimality is very close to the proposed principle of Maximum Entropy Production and a range of other proposed principles related to thermodynamics, such as fastest depletion of gradients [38] or maximizing "access" [102–104]. One aspect that stands out regarding the proposed MEP principle is that substantial progress has been made in recent years to develop the theoretical foundation [105–108]. This theoretical foundation uses the MaxEnt inference method from information theory [109,110], which is the well-established basis for equilibrium statistical mechanics and is used to derive equilibrium thermodynamics from this assumption. In simple terms, the MaxEnt procedure yields us the best, least biased prediction for a given set of constraints. Since for Earth system processes energy and mass balances always apply at a minimum, the MaxEnt approach yields us the usual Lagrange multipliers of temperature and chemical potentials of equilibrium thermodynamics, so that in practice MaxEnt should translate in maximizing thermodynamic entropy production [111]. When dealing with Newtonian mechanics, then it may well be that the inclusion of the constraints of momentum conservation into the MaxEnt algorithm yield maximum power and dissipation as a result (Dewar, pers. comm.). This aspect would need further investigations.

The work presented here addresses some of the critics formulated against the proposed MEP principle [112–115]. These criticisms include the claim that MEP assumes teleology (i.e. that the process would need to "know" what it has to do to maximize, just like the most common objection to the Gaia hypothesis, see above) and that MEP does not tell us which entropy production to maximize. To respond to the first criticism, the work here shows by simple means that power generation is limited by maximum efficiencies, and these limits are fundamental and constrain the dynamics that are driven by the power generated. The existence of a maximum in power generation does not necessarily imply that the dynamics in fact utilize the maximally extractable power. The energy-, mass and other balance constraints are compatible with a full range of possible dynamics that do not need to maximize power extraction. This is where the MaxEnt algorithm comes in. The MaxEnt algorithm tells us that the different sets of possible dynamics that are compatible with the balance constraints are not all equally as likely. It is then not teleology, but a matter of highest probability that the generalities observed in the macroscopic dynamics are associated with the maximum in power generation. The second criticism is hopefully clarified to some extent by the hierarchical view of power generation and transfer in that it puts some order in our understanding of which thermodynamic variable causes which other variable to evolve away from equilibrium, and what the consequence of that disequilibrium is on the driver. It is through this hierarchy of power generation and transfer that the planetary rates of entropy production can be enhanced. The extent to which planetary entropy production can be enhanced is then limited by the maximum thermodynamic efficiencies along the hierarchy.

Last, but not least, this work corrects and clarifies some earlier notions on the relationship between Maximum Entropy Production and states of minimum entropy [116,57,117].

7.2. Implications

The hierarchical view of the Earth system has implications for how we should model the Earth system, how we can get a holistic description of it that should help us to reconstruct past environments and its evolution in time, and how we should view and evaluate future change due to human activity within the system.

While energy and mass conservation are the basis of practically all Earth system models, the work balance is typically not considered and neither is the hierarchical transfer of power among processes. The latter aspect is likely where the largest shortcomings are found in Earth system models. To give one example: Atmospheric models typically simulate dissipation of kinetic energy in the boundary layer using semi-empirical parameterizations with no-slip boundary conditions. When we think about wind blowing over the ocean or over the forest floor in autumn, then some of this wind is not dissipated in the turbulent cascade, but rather work is extracted that generates waves or lifts leaves off the ground, thereby generating potential energy. This transfer of power can be quite considerable: It is estimated that of the approx. 450 TW of kinetic energy that is dissipated near the surface [46], about 60 TW is used to generate ocean waves [22]. It is likely that such power transfer processes are not adequately represented in current boundary layer parameterization schemes, resulting in biases in the turbulent heat fluxes, which are linked to the extent of momentum dissipation and their sensitivity to change. The same may hold true in general terms about the coupling of all kinds of thermodynamic variables within Earth system models, leading to the suspicion that these models may not be thermodynamically consistent in the very relevant areas at which interactions take place.

The hierarchy shown in Fig. 11 describes the interrelationship of different variables of the Earth system as a function of the ability to generate power. By this, the hierarchy essentially provides a holistic description of the planetary environment. This basis should help us to get a fuller description and understanding of past environments since it shows that many of the variables are not independently driven, but strongly connected by hierarchical power generation and transfer. Hence, this should possibly form the basis to better understand past environments and relate evolutionary trends to changes in power generation [118,116].

The work budget quantified here and shown in Table 3 clearly shows how human activity is part of the Earth system. We are sustained by food supplied by the productivity of the biosphere and we use mostly fossil fuels to sustain our industrial activities. The power associated with meeting our needs for free energy to satisfy our metabolic and industrial requirements are of significant magnitude, essential to maintain civilization [119], and limited by characteristic maxima [120,121]. The work budget shown in Table 3 shows that human dissipation taken together is more than all power generated and dissipated by geologic processes! Hence, the notion that humans now act as a geologic force is similar to Vernadsky's notion [1] and consistent with Crutzen coining the present era as the geologic era of the anthropocene [122].

When it comes to present issues of global change, one aspect we know very little about is how aspects of global change affect the natural ability of the Earth system to generate power. One example is the potential replacement of human needs for fossil fuels by renewable power generation. If the human demand for power is met by large-scale deployment of wind turbines, kinetic energy is extracted from the lower atmosphere to generate electric power. This extraction is limited by thermodynamic efficiencies as shown in Section 4.7 and inevitably leaves less free energy in the atmosphere [123], therefore this should result in a weakening of the power transfer within the hierarchy. On the other hand, the utilization of solar power can convert incoming shortwave radiation into electric energy that would otherwise be "wasted" by the conversion into heat. Hence, solar power has the ability to enhance power generation. It would seem essential and urgent to understand the whole range of global challenges in this context. It would allow us to distinguish among global changes that weaken power generation within the Earth system as opposed to those effects that have the ability to enhance power generation.

When we think about global change in a broader context and take the reformulated Gaia hypothesis of the previous section as being valid for a moment, we could then argue that in the past the evolution of life has found various ways to extract and utilize solar power more and more efficiently, thereby empowering Earth system processes. It would then seem to be a logical extension to argue that humans are to continue this evolutionary trend with their own ideas and increase power generation on the planet even further, thereby "empowering" the future. This extrapolation of the reformulated Gaia hypothesis to the future of humans in the Earth system provides a positive outlook and an alternative to Lovelock's recent, very grim view on the planetary future [124].

8. Synthesis and outlook

Thermodynamics has existed for a long time, but its rigorous application to life and Earth system functioning has been surprisingly absent. Based on Lovelock's important observation from 45 years ago that atmospheric chemical disequilibrium is a sign for widespread life on the planet, this paper has developed a theory of how disequilibrium is maintained in steady state for Earth system variables by the generation and transfer of power within a hierarchy of processes. This thermodynamic basis was then used to determine that photosynthetic life contributes about two orders of magnitude more geochemical power to Earth system processes than purely abiotic processes. This then substantiates Lovelock's notion of the pivotal role that life plays in shaping the chemical disequilibrium of the Earth's atmosphere. In addition, there are several indications that suggest that power generation and transfer is maximized within this hierarchy and for biotic activity, resulting in planetary conditions that are possibly maintained in a state furthest away from equilibrium yet maximizing entropy production at the same time.

This hierarchical, thermodynamic theory of Earth developed here has far-reaching implications. It places interactions between processes – be it among physical processes, or between life and its environment – into a context of hierarchical transfer of power, disequilibrium, emergent dynamics and its associated effects. This should reveal novel insights on the operation of such interactions. Furthermore, the interconnectedness of different environmental variables within the hierarchy should help us to get a better, holistic reconstruction of past environmental conditions.

In light of the human effects on the planet, the view developed here quantifies the significant role that humans play in terms of dissipating substantial amounts of free energy, which are of the same order as all power generated by geologic processes. The focus on power generation developed here should allow us to better understand the consequences associated with human activity on the natural power sources within the Earth system. Even more, it should enable us to prevent weakening the natural power sources, and point out possible directions to develop and employ technologies that are able to empower the future of the planet.

Acknowledgements

The author thanks the members of the Biospheric Theory and Modelling group for stimulating discussions on various aspects of the material contained in this paper, Fabian Gans for help with analytical solutions of some of the differential equations, Ryan Pavlick for estimates on work by desalination, Roderick Dewar for discussions on the relationship of MEP and states of minimum entropy, and the Helmholtz Alliance "Planetary Evolution and Life" for funding.

Appendix A. Simple momentum balance model

To analytically solve the simple momentum balance model, we introduce a new variable $\Delta v = v_h - v_l$ and rewrite the coupled differential equations for the momentum balances (Eqs. (35)) as

$$\rho_e \cdot \frac{d(\Delta v)}{dt} = F_{acc} - k_{mom} \cdot \Delta v \tag{53}$$

with an equivalent density $\rho_e = \rho_l \rho_h / (\rho_l + \rho_h)$. Using momentum conservation, $\rho_h v_h + \rho_l v_l = 0$, the individual velocities are given by:

$$v_h = \frac{\rho_l}{\rho_h + \rho_l} \cdot \Delta v, \qquad v_l = \frac{\rho_h}{\rho_h + \rho_l} \cdot \Delta v \tag{54}$$

The solution of the differential equation is:

$$\Delta v(t) = \Delta v_f + (\Delta v_0 - \Delta v_f) \cdot \exp(-k_{mom}/\rho_e \cdot t)$$
(55)

where Δv_0 is the initial velocity gradient and $\Delta v_f = F_{acc}/k_{mom}$ is the final gradient for $t \to \infty$. The expressions for the free energy A_{mom} and the disequilibrium entropy S_{mom} are given by:

$$\frac{dA_{mom}}{dt} = -T \cdot \frac{dS_{mom}}{dt} = P_{in}(t) - D(t)$$
(56)

Integration of the two terms are done separately over a time interval Δt . To calculate $\int P_{in} dt$, we get (assuming that the accelerating force F_{acc} remains approximately constant over Δt):

$$\int_{0}^{\Delta t} P_{in} dt = F_{acc} \cdot \int_{0}^{\Delta t} (\Delta v) dt$$
$$= F_{acc} \Delta v_f \Delta t - \rho_e \Delta v_f (\Delta v_f - \Delta v_0) [1 - \exp(-k_{mom}/\rho_e \Delta t)]$$
(57)

The dissipation of momentum by the momentum flux J_{mom} is given by:

$$D_{mom} = J_{mom} \cdot (v_h - v_l) = k_{mom} (\Delta v)^2$$
(58)

Integration over ΔT yields:

$$\int_{0}^{\Delta t} D_{mom} dt = k_{mom} \cdot \int_{0}^{\Delta t} (\Delta v)^2 dt$$
$$= k_{mom} (\Delta v_f)^2 \Delta t - 2\rho_e \Delta v_f (\Delta v_f - \Delta v_0) [1 - \exp(-k_{mom}/\rho_e \Delta t)]$$
$$+ \frac{\rho_e (\Delta v_0 - \Delta v_f)^2}{2} [1 - \exp(-2k_{mom}/\rho_e \Delta t)]$$
(59)

Taken together, the free energy A_{mom} is given by:

$$A_{mom}(\Delta t) = \int_{0}^{\Delta t} P_{in} - D_{mom} dt$$

= $\rho_e \Delta v_f (\Delta v_f - \Delta v_0) [1 - \exp(-k_{mom}/\rho_e \Delta t)]$
 $- \frac{\rho_e (\Delta v_0 - \Delta v_f)^2}{2} [1 - \exp(-2k_{mom}/\rho_e \Delta t)]$ (60)

Note that for $t \to \infty$ and $\Delta v_0 = 0$ this expression yields

$$A_{mom,f} = \frac{\rho_e}{2} \cdot (\Delta v_f)^2 \tag{61}$$

which is the well-known expression for kinetic energy.

Appendix B. Maximum power of vertical gradients

A similar model to the one used in Sections 2.3 and 4.4 is used here to estimate the maximum power of a vertical gradient in temperature. The energy balances of the surface and the atmosphere are written as:

$$J_{in} - J_{rad} - J_{ex} = 0, \qquad J_{rad} - J_{out} + J_{ex} = 0$$
(62)

where J_{in} is the surface heating, J_{rad} is the radiative exchange between the surface and the atmosphere, J_{ex} the extracted heat flux to derive power, and J_{out} the radiative cooling of the atmosphere. The radiative exchange is linearized as a function of the temperature gradient between the surface and the atmosphere as $J_{rad} = k_{rad}(T_s - T_a)$, with k_{rad} being an effective, "radiative" conductivity. Blackbody emission is used to describe the radiative loss from the atmosphere, $J_{out} = \sigma T_a^4$. In steady state, a given absorption of J_{in} at the surface is balanced by the net radiative loss from the atmosphere, $J_{in} = J_{out}$, and hence the temperature T_a is fixed to $T_a = (J_{out}/\sigma)^{1/4}$.

The temperature difference between the surface and the atmosphere, $\Delta T = T_s - T_a$ is hence given by:

$$\Delta T = (J_{in} - J_{ex})/k_{rad} \tag{63}$$

with a temperature gradient $\Delta T_0 = J_{in}/k_{rad}$ in the absence of extracted work ($J_{ex} = 0$).

The net entropy exchange *NEE* of the system is described by an influx of heat J_{in} at a temperature T_s and a loss of heat $J_{out} = J_{in}$ at temperature T_a :

$$NEE = J_{in} \cdot \left(\frac{1}{T_a} - \frac{1}{T_s}\right) \tag{64}$$

The net entropy exchange of a potential heat engine that is fueled by the temperature difference $T_s - T_a$ and the heat flux J_{ex} , is maximized when:

$$NEE_{ex} = J_{ex} \cdot \left(\frac{1}{T_a} - \frac{1}{T_s}\right) = J_{ex} \cdot \frac{\Delta T}{T_s T_a} = \frac{J_{ex} \cdot (J_{in} - J_{ex})}{k_{rad} T_s T_a}$$
(65)

This entropy exchange is balanced by the generation and dissipation of power within the engine, i.e. $NEE = P/T_a = D/T_a$. This expression is maximized for $J_{ex,opt} = J_{in}/2$. At this flux, the temperature gradient reduces to a value of $\Delta T_{opt} = \Delta T_0/2$, and the overall maximum extractable power P_{max} is:

$$P_{max} = \frac{1}{4} \cdot \frac{\Delta T_0}{T_s} \cdot J_{in} \tag{66}$$

With a surface heating of about half of the incoming solar flux of $\approx 170 \text{ W m}^{-2}$, and typical temperatures of $T_s = 288 \text{ K}$ and $T_a = 255 \text{ K}$, one obtains an efficiency of about 11.4% or maximum power of $P_{max} = 9.7 \text{ W m}^{-2}$. However, some of this power is consumed by generating and dissipating potential energy and lifting moisture that does not result in motion.

Appendix C. Maximum power in temporal variations

1.....

To estimate the maximum power extractable from a temporally varying source of radiative heating, we consider the simplest form of a step-wise function, in which the flux of solar radiation J_{sw} varies by $+/-\Delta J_{sw}$ for a period τ :

$$J_{sw} = J_{sw,0} + \begin{cases} \Delta J_{sw}, & t \leq \tau/2 \\ -\Delta J_{sw}, & t \geq \tau/2 \end{cases}$$
(67)

The skin temperature of the surface, T_s , is given by the local energy balance, in which we neglect heat storage changes:

$$c_s \frac{dI_s}{dt} = J_{sw} - J_{lw} - J_{ex} \approx 0 \tag{68}$$

where J_{lw} is the radiative cooling of the surface by net emission of longwave radiation (parameterized as $J_{lw} = a + b \cdot T_s$, as above), and J_{ex} is the heat flux removed to drive the heat engine. Using the parameterization of J_{lw} , we then obtain the expression for the variation in temperature $\pm \Delta T_s$ around the mean temperature $T_{s,0} = (J_{sw,0} - a)/b$:

$$\Delta T_s = \frac{\Delta J_{sw} - J_{ex}}{b} \tag{69}$$

The heat flux J_{ex} feeds a heat reservoir with temperature T_d , for which we assume an infinite heat capacity, so that the working temperature is constant ($T_d = T_{s,0}$). The total entropy exchanged *NEE* between the skin temperature and the reservoir over a time period τ is:

$$NEE = J_{ex} \cdot \left(\frac{1}{T_{s,0} + \Delta T_s} - \frac{1}{T_{s,0} - \Delta T_s}\right)$$
(70)

Assuming that this entropy exchange results from power extraction and subsequent dissipation, i.e. $NEE = D/T_{s,0} = P/T_{s,0}$, we get for the extractable power *P*:

$$P \approx J_{ex} \cdot \frac{\Delta T_s}{T_{s,0}} = \frac{J_{ex} \cdot (\Delta J_{sw} - J_{ex})}{b \cdot T_{s,0}}$$
(71)

This expression has a maximum at a flux $J_{ex} = \Delta J_{sw}/2$, at which the temperature variation $\Delta T_s = \Delta T_s (J_{ex} = 0)/2$, so that the overall, maximum extractable power is given by:

$$P_{max} = \frac{1}{4} \cdot \frac{\Delta T_s(J_{ex} = 0)}{T_{s,0}} \cdot \Delta J_{sw}$$
(72)

References

- [1] Vernadski VI. Biosfera (The biosphere). Leningrad: Nauka; 1926 [translated and reprinted in 1998 by Springer, New York].
- [2] Lovelock JE. A physical basis for life detection experiments. Nature 1965;207:568-70.
- [3] Hayes JM, Waldbauer JR. The carbon cycle and associated redox processes through time. Philos Trans Roy Soc London Ser B 2006;361:931– 50.
- [4] Dietrich WE, Perron JT. The search for a topographic signature of life. Nature 2006;439:411-8.
- [5] Kleidon A, Fraedrich K, Heimann M. A green planet versus a desert world: Estimating the maximum effect of vegetation on land surface climate. Clim Ch 2000;44:471–93.
- [6] Kleidon A. Testing the effect of life on Earth's functioning: How Gaian is the Earth system? Clim Ch 2002;66:271–319.
- [7] Lenton TM. Gaia and natural selection. Nature 1998;394:439-47.
- [8] Schwartzman DW, Volk T. Biotic enhancement of weathering and the habitability of Earth. Nature 1989;340:457-60.
- [9] Rosing MT, Bird DK, Sleep NH, Glassley W, Albarede F. The rise of continents an essay on the geologic consequences of photosynthesis. Paleogeogr Paleoclimatol Paleoecol 2006;232:99–113.
- [10] Lenton TM, Schellnhuber HJ, Szathmary E. Climbing the co-evolutionary ladder. Nature 2004(431):913.
- [11] Eddington AS. The nature of the physical world. Macmillan; 1928.
- [12] Lorenz EN. Available potential energy and the maintenance of the general circulation. Tellus 1955;7:157-67.
- [13] Paltridge GW. The steady-state format of global climate. Q J Roy Meteor Soc 1978;104:927–45.
- [14] Lorenz RD, Lunine JI, Withers PG, McKay CP. Titan, Mars and Earth: Entropy production by latitudinal heat transport. Geophys Res Lett 2001;28:415–8.
- [15] Kleidon A, Fraedrich K, Kunz T, Lunkeit F. The atmospheric circulation and states of maximum entropy production. Geophys Res Lett 2003;30:2223. doi:10.1029/2003GL018363.
- [16] Emanuel KA. Thermodynamic control of hurricane intensity. Nature 1999;401:665-9.
- [17] Edlefsen NE, Anderson ABC. Thermodynamics of soil moisture. Hilgardia 1943;15:31-298.
- [18] Leopold LB, Langbein WL. The concept of entropy in landscape evolution. U.S. Geol. Surv. Prof. Pap. 252.
- [19] Pauluis O, Held IM. Entropy budget of an atmosphere in radiative convective equilibrium. Part I: Maximum work and frictional dissipation. J Atmos Sci 2002;59:126–39.
- [20] Pauluis O, Held IM. Entropy budget of an atmosphere in radiative convective equilibrium. Part II: Latent heat transport and moist processes. J Atmos Sci 2002;59:140–9.
- [21] Munk W, Wunsch C. Abyssal recipes II: Energetics of tidal and wind mixing. Deep-Sea Res 1998;45:1977–2010.
- [22] Ferrari R, Wunsch C. Ocean circulation kinetic energy: reservoirs, sources, and sinks. Annu Rev Fluid Mech 2009;41:253-82.
- [23] Ozawa H, Ohmura A, Lorenz RD, Pujol T. The second law of thermodynamics and the global climate system a review of the Maximum Entropy Production principle. Rev Geophys 2003;41:1018.
- [24] Kleidon A, Lorenz RD, editors. Non-equilibrium thermodynamics and the production of entropy: life, Earth, and beyond. Heidelberg, Germany: Springer Verlag; 2005.
- [25] Martyushev LM, Seleznev VD. Maximum entropy production principle in physics, chemistry and biology. Phys Rep 2006;426(1):1–45.

- [26] Kleidon A. Non-equilibrium thermodynamics and Maximum Entropy Production in the Earth system: applications and implications. Naturwissenschaften 2009;96:653–77.
- [27] Kleidon A, Malhi Y, Cox PM. Maximum entropy production in environmental and ecological systems. Philos Trans Roy Soc London Ser B 2010;365:1297–302.
- [28] Boltzmann L. Der zweite Hauptsatz der mechanischen Wärmetheorie. Almanach d kais Akad d Wiss 1886;36:225-59.
- [29] Schrödinger E. What is life? The physical aspect of the living cell. Cambridge, UK: Cambridge University Press; 1944.
- [30] Lovelock JE, Margulis L. Atmospheric homeostasis by and for the biosphere: The Gaia hypothesis. Tellus 1974;26:2-10.
- [31] Lotka AJ. Contribution to the energetics of evolution. Proc Natl Acad Sci USA 1922;8:147-51.
- [32] Lotka AJ. Natural selection as a physical principle. Proc Natl Acad Sci USA 1922;8:151–4.
- [33] Odum EP. The strategy of ecosystem development. Science 1969;164:262-70.
- [34] Odum HT. Self-organization, transformity, and information. Science 1988;242:1132-9.
- [35] Ulanowicz RE, Hannon BM. Life and the production of entropy. Proc Roy Soc London Ser B 1987;232:181–92.
- [36] Schneider ED, Kay JJ. Life as a manifestation of the second law of thermodynamics. Math Comput Model 1994;19:25-48.
- [37] Kleidon A. Beyond Gaia, Thermodynamics of life and Earth system functioning. Clim Ch 2004;66:271–319.
- [38] Schneider ED, Sagan D. Into the cool: energy flow, thermodynamics and life. University of Chicago Press; 2005.
- [39] Dewar RC. Maximum entropy production and plant optimization. Phil Trans Roy Soc London Ser B 2010;365:1429–35.
- [40] Lovelock JE. Gaia as seen through the atmosphere. Atmos Environ 1972;6:579-80.
- [41] Lovelock JE. Gaia: a new look at life on Earth. Oxford, UK: Oxford University Press; 1972.
- [42] Aoki I. Entropy productions on the Earth and other planets of the solar system. J Phys Soc Japan 1983;52(3):1075-8.
- [43] Peixoto JP, Oort AH, de Almeida M, Tome A. Entropy budget of the atmosphere. J Geophys Res 1991;96:10,981-8.
- [44] Goody R. Sources and sinks of climate entropy. Q J Roy Meteor Soc 2000;126(566):1953-70.
- [45] Kondepudi D, Prigogine I. Modern thermodynamics from heat engines to dissipative structures. Chichester: Wiley; 1998.
- [46] Peixoto JP, Oort AH. Physics of climate. New York, NY: American Institute of Physics; 1992.
- [47] Hartmann DL. Global physical climatology. San Diego, CA: Academic Press; 1994.
- [48] Ozawa H, Ohmura A. Thermodynamics of a global-mean state of the atmosphere a state of maximum entropy increase. J Clim 1997;10:441– 5.
- [49] Pujol T, Fort J. States of maximum entropy production in a one-dimensional vertical model with convective adjustment. Tellus 2002;54(4):363–9.
- [50] Pujol T. Eddy heat diffusivity at maximum dissipation in a radiative-convective one-dimensional climate model. J Met Soc Japan 2003;81(2):305–15.
- [51] Lorenz RD, Mckay CP. A simple expression for vertical convective fluxes in planetary atmospheres. Icarus 2003;165(2):407–13.
- [52] Vanyo JP, Paltridge GW. A model for energy dissipation at the mantle-core boundary. Geophys J 1981;66(3):677-90.
- [53] Lorenz RD. Planets, life and the production of entropy. Int J Astrobiol 2002;1:3-13.
- [54] Dyke JG, Gans F, Kleidon A. Assessing potential biotic effects on the interior dynamics of planet Earth using non-equilibrium thermodynamics. Earth Syst Dyn Discuss 2010;1:191–246. <u>doi:10.5194/esdd-1-191-2010</u>. www.earth-syst-dynam-discuss.net/1/191/2010/.
- [55] Kagan BA, Sündermann J. Dissipation of tidal energy, paleotides, and evolution of the Earth-Moon system. Adv Geophys 1996;38:179–266.
- [56] Pauluis O. Water vapor and entropy production in the Earth's atmosphere. In: Kleidon A, Lorenz RD, editors. Non-equilibrium thermodynamics and the production of entropy: life, Earth, and beyond. Heidelberg, Germany: Springer Verlag; 2005. p. 173–90.
- [57] Kleidon A. A basic introduction to the thermodynamics of Earth system far from equilibrium and maximum entropy production. Phil Trans Roy Soc London Ser B 2010;365:1303–15.
- [58] Lenardic A, Moresi L-N, Jellinek AM, Manga M. Continental insulation, mantle cooling, and the surface area of oceans and continents. EPSL 2005;234:317–33.
- [59] Bering III EA, Few AA, Benbrook JR. The global electric circuit. Phys Today 1998:24-30.
- [60] Herrmann HJ. Aeolian transport and dune formation. Lecture Notes in Phys 2007;705:363–86.
- [61] Li L, Ingersoll AP, Jiang X, Feldman D, Yung YL. Lorenz energy cycle of the global atmosphere based on reanalysis datasets. Geophys Res Lett 2007;34:L16813.
- [62] Fraedrich K, Jansen H, Kirk E, Luksch U, Lunkeit F. The planet simulator: towards a user friendly model. Z Meteorol 2005;14:299-304.
- [63] Pauluis O, Balaji V, Held IM. Frictional dissipation in a precipitating atmosphere. J Atmos Sci 2000;57:987–94.
- [64] Isaacs JD, Schmitt WR. Ocean energy: forms and prospects. Science 1980;207:265–73.
- [65] Schlesinger WH. Biogeochemistry: an analysis of global change. Academic Press; 1997.
- [66] Vitousek PM, Ehrlich PR, Ehrlich AH, Matson PA. Human appropriation of the products of photosynthesis. Bioscience 1986;36:368-73.
- [67] Rojstaczer S, Sterling SM, Moore NJ. Human appropriation of photosynthesis products. Science 2001;294:2549–52.
- [68] Imhoff ML, Bounoua L, Ricketts T, Loucks C, Harriss R, Lawrence WT. Global patterns in human consumption of net primary production. Nature 2004;429:870–3.
- [69] International energy outlook. Tech. rep.. Energy Information Administration, US Dept. of Energy, Energy Information Administration; 2009.
- [70] Lorenz EN. Generation of available potential energy and the intensity of the general circulation. In: Pfeffer RC, editor. Dynamics of climate. Oxford, UK: Pergamon Press; 1960. p. 86–92.
- [71] Paltridge GW. Global dynamics and climate a system of minimum entropy exchange. Q J Roy Meteor Soc 1975;101:475-84.
- [72] Paltridge GW. Climate and thermodynamic systems of maximum dissipation. Nature 1979;279:630–1.
- [73] Lorenz RD. The two-box model of climate: limitations and applications to planetary habitability and maximum entropy production studies. Philos Trans Roy Soc London Ser B 2010;365:1349–54.
- [74] Kleidon A, Fraedrich K, Kirk E, Lunkeit F. Maximum entropy production and the strength of boundary layer exchange in an atmospheric general circulation model. Geophys Res Lett 2006;33:L06706. <u>doi:10.1029/2005GL025373</u>.

- [75] Ozawa H, Ohmura A. Thermodynamics of a global-mean state of the atmosphere a state of maximum entropy increase. J Clim 1997;10(3):441–5.
- [76] Jupp TE, Cox PM. Mep and planetary climates: insights from a two-box climate model containing atmospheric dynamics. Philos Trans Roy Soc London Ser B 2010;365:1355–65.
- [77] Jupp TE, Schultz A. Physical balances in subseafloor hydrothermal convection cells. J Geophys Res 109. Article number B05101. doi:10.1029/2003JB002697.
- [78] Malkus WVR. The heat transport and spectrum of thermal turbulence. Proc Roy Soc London Ser A 1954;225:196-212.
- [79] Malkus WVR. Outline of a theory of turbulent shear flow. J Fluid Mech 1956;1:521-39.
- [80] Busse FH. Eine neuartige Methode zur theoretischen Behandlung turbulenter Transportvorgänge. Z Angew Math Mech 1968;48:T187-90.
- [81] Busse FH. Bounds for turbulent shear flow. J Fluid Mech 1970;41:219-40.
- [82] Ozawa H, Shimokawa S, Sakuma H. Thermodynamics of fluid turbulence: A unified approach to the maximum transport properties. Phys Rev E 2001;6402(2):026303.
- [83] Rasmussen C, Southard RJ, Horwath WJ. Modeling energy inputs to predict pedogenic environments using regional environmental databases. Soil Sci Soc Am J 2005;69:1266–74.
- [84] Rasmussen C, Tabor N. Application of a quantitative pedogenic energy model across a range of environmental gradients. Soil Sci Soc Am J 2007;71:1719–29.
- [85] Kleidon A, Schymanski S. Thermodynamics and optimality of the water budget on land: A review. Geophys Res Lett 2008;35:L20404.
- [86] Zehe E, Blume T, Blöschl G. The principle of maximum energy dissipation: a novel thermodynamic perspective on rapid water flow in connected soil structures. Philos Trans Roy Soc London Ser B 2010;365:1377–86.
- [87] Lin H. Linking principles of soil formation and flow regimes. Soil architecture and preferential flow across scales, 27 October 2010. J Hydrol 2010;393(1–2):3–19. doi:10.1016/j.jhydrol.2010.02.013. ISSN 0022-1694.
- [88] Rinaldo A, Rodriguez-Iturbe I, Rigon R, Ijjasz-Vasquez E, Bras RL. Self-organized fractal river networks. Phys Rev Lett 1993;70(6):822–5. doi:10.1103/PhysRevLett.70.822.
- [89] Rinaldo A, Maritan A, Colaiori F, Flammini A, Rigon R, Rodriguez-Iturbe I, et al. Thermodynamics of fractal networks. Phys Rev Lett 1996;76(18):3364–7.
- [90] Rodriguez-Iturbe I, Rinaldo A. Fractal river basins: chance and self-organization. Cambridge, UK: Cambridge University Press; 2001.
- [91] Rodriguez-Iturbe I, Rinaldo A, Rigon R, Bras RL, Ijjasz-Vsaquez E, Marani A. Fractal structures as least energy patterns: the case of river networks. Geophys Res Lett 1992;19:889–92.
- [92] Rodriguez-Iturbe I, Rinaldo A, Rigon R, Bras RL, Marani A, Ijjasz-Vsaquez E. Energy dissipation, runoff production, and the threedimensional structure of river basins. Water Resour Res 1992;28:1095–103.
- [93] Kleidon A, Heimann M. A method of determining rooting depth from a terrestrial biosphere model and its impacts on the global water- and carbon cycle. Glob Change Biol 1998;4:275–86.
- [94] Kleidon A, Heimann M. Optimised rooting depth and its impacts on the simulated climate of an atmospheric general circulation model. Geophys Res Lett 1998;25:345–8.
- [95] Kleidon A. Global datasets of rooting zone depth inferred from inverse methods. J Clim 2004;17:2714-22.
- [96] Kleidon A. Optimized stomatal conductance of vegetated land surfaces and its effects on simulated productivity and climate. Geophys Res Lett 2004;31:L21203. doi:10.1029/2004GL020769.
- [97] Kleidon A. Optimized stomatal conductance and the climate sensitivity to carbon dioxide. Geophys Res Lett 2007;34:L14709. doi:10.1029/2007GL030342.
- [98] Schneider SH, Boston PJ, editors. Scientists on Gaia. Cambridge, Mass.: MIT Press; 1991.
- [99] Schneider SH, Miller JR, Crist E, Boston PJ, editors. Scientists debate Gaia: The next century. Cambridge, MA: MIT Press; 2004.
- [100] Kirchner JW. The Gaia hypothesis: Can it be tested? Rev Geophys 1989;27:223-35.
- [101] Kirchner JW. The Gaia hypothesis: Fact, theory, and wishful thinking. Clim Ch 2002;52:391-408.
- [102] Bejan A, Lorente S. Constructal theory of generation of configuration in nature and engineering. J Appl Phys 2006;100(4):041301.
- [103] Bejan A, Marden JH. The constructal unification of biological and geophysical design. Phys Life Rev 2009;6:85–102.
- [104] Bejan A, Lorente S. The constructal law of design and evolution in nature. Philos Trans Roy Soc London Ser B 2010;365:1335–47.
- [105] Dewar RC. Information theory explanation of the fluctuation theorem, Maximum Entropy Production, and self-organized criticality in nonequilibrium stationary states. J Phys A 2003;36:631–41.
- [106] Dewar RC. Maximum Entropy Production and non-equilibrium statistical mechanics. In: Kleidon A, Lorenz RD, editors. Non-equilibrium thermodynamics and the production of entropy: life, Earth, and beyond. Heidelberg, Germany: Springer Verlag; 2005.
- [107] Dewar RC. Maximum entropy production and the fluctuation theorem. J Phys A 2005;38:L371-81. doi:10.1088/0305-4470/38/21/L01.
- [108] Dewar RC. Maximum entropy production as an inference algorithm that translates physical assumptions into macroscopic predictions: don't shoot the messenger. Entropy 2010;11(4):931–44.
- [109] Jaynes ET. Information theory and statistical mechanics. Phys Rev 1957;106(4):620-30.
- [110] Jaynes ET. Information theory and statistical mechanics. II. Phys Rev 1957;108(2):171-90.
- [111] Dyke J, Kleidon A. The maximum entropy production principle: Its theoretical foundations and applications to the Earth system. Entropy 2010;12(3):613–30.
- [112] Rodgers CD. Minimum entropy exchange principle reply. Q J Roy Meteor Soc 1976;102:455-7.
- [113] Volk T. The properties of organisms are not tunable parameters selected because they create maximum entropy production on the biosphere scale: A by-product framework in response to Kleidon. Clim Ch 2007;85:251–8.
- [114] Caldeira K. The maximum entropy principle: a critical discussion. Clim Ch 2007;85:267–9.
- [115] Volk T, Pauluis O. It is not the entropy you produce, rather, how you produce it. Philos Trans Roy Soc London Ser B 2010;365:1317-22.

- [116] Kleidon A. Non-equilibrium thermodynamics, Maximum Entropy Production, and Earth system evolution. Philos Trans Roy Soc London Ser A 2010;368:181–96.
- [117] Paltridge GW. A story and a recommendation about the principle of maximum entropy production. Entropy 2009;11:945-8.
- [118] Kleidon A. Maximum Entropy Production and general trends in biospheric evolution. Paleontol J 2009;43:130-5.
- [119] Garrett TJ. Are there basic physical constraints on future anthropogenic emissions of carbon dioxide? Clim Change (2009) doi:10.1007/s10584-009-9717-9.
- [120] Kleidon A. The climate sensitivity to human appropriation of vegetation productivity and its thermodynamic characterization. Glob Planet Ch 2006;54:109–27.
- [121] Kleidon A. Climatic constraints on maximum possible levels of human activity and their relation to human evolution and global change. Clim Ch 2009;95:405–31.
- [122] Crutzen PJ. Geology of mankind. Nature 2002;415:23.
- [123] Miller LM, Gans F, Kleidon A. Estimating maximum global land surface wind power extractability and associated climatic consequences. Earth Syst Dynam Discuss 2010;1:169–89. doi:10.5194/esdd-1-169-2010. www.earth-syst-dynam-discuss.net/1/169/2010/.
- [124] Lovelock JE. The vanishing face of Gaia: a final warning. Basic Books; 2009.