Chapter 1
Beyond the Second Law: An Overview

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Abstract The Second Law of Thermodynamics governs the average direction of all non-equilibrium dissipative processes. However it tells us nothing about their actual rates, or the probability of fluctuations about the average behaviour. The last few decades have seen significant advances, both theoretical and applied, in understanding and predicting the behaviour of non-equilibrium systems beyond what the Second Law tells us. Novel theoretical perspectives include various extremal principles concerning entropy production or dissipation, the Fluctuation Theorem, and the Maximum Entropy formulation of non-equilibrium statistical mechanics. However, these new perspectives have largely been developed and applied independently, in isolation from each other. The key purpose of the present book is to bring together these different approaches and identify potential connections between them: specifically, to explore links between hitherto separate theoretical concepts, with entropy production playing a unifying role; and to close the gap between theory and applications. The aim of this overview chapter is to orient and guide the reader towards this end. We begin with a rapid flight over the fragmented landscape that lies beyond the Second Law. We then highlight the connections that emerge from the recent work presented in this volume. Finally we summarise these connections in a tentative road map that also highlights some directions for future research.

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R. C. Dewar et al. (eds.), *Beyond the Second Law*,
Understanding Complex Systems, DOI: 10.1007/978-3-642-40154-1_1,

1.1 The Challenge: Understanding and Predicting Non-equilibrium Behaviour

Non-equilibrium,[1] dissipative systems abound in nature. Examples span the biological and physical worlds, and cover a vast range of scales: from biomolecular motors, living cells and organisms to ecosystems and the biosphere; from turbulent fluids and plasmas to hurricanes and planetary climates; from growing crystals and avalanches to earthquakes; from cooling coffee cups to economies and societies; from stars and supernovae to clusters of galaxies and beyond.

A characteristic feature of all open, non-equilibrium systems is that they import energy and matter from their surroundings in one form and re-export it in a more degraded (higher entropy) form. A sheared viscous fluid driven out of thermodynamic equilibrium by the external input of kinetic energy eventually dissipates and expels that energy to its environment as heat; the Earth absorbs short-wave radiation at solar temperatures and re-emits it to space as long-wave radiation at terrestrial temperatures; living organisms use the chemical free energy ultimately derived from photons to grow and survive, eventually dissipating it to their environment as heat and carbon dioxide.

In association with these exchanges of energy and matter, spatial gradients in temperature and chemical concentration are set up and maintained, both internally and between the system and its environment. The patterns of flows and their associated gradients self-organize into intricate dynamical structures that continually transport and transform energy and mass into higher entropy forms: thus emerge plant vascular systems, food webs, river networks, and turbulent eddies such as Jupiter's Red Spot and the convective cells on the Sun's surface. Idealised systems in equilibrium with their surroundings exhibit no flows or gradients; they appear static, structureless, lifeless. In stark contrast, non-equilibrium systems, even purely physical ones, appear to be alive in a sense that perhaps even defines life itself, at least thermodynamically [1].

In view of their ubiquity in nature, understanding and predicting the behaviour of non-equilibrium systems lies at the heart of many questions of fundamental and practical importance, from the origin of a low entropy universe and the evolution of life, to the development of nanotechnology and the prediction of climate change. What is life? And what are the general requirements for its emergence on Earth and elsewhere? What determines the rate at which the universe tends towards thermodynamic equilibrium? How is the functioning of nanoscale devices affected by molecular-scale fluctuations in energy and mass flow? How will the large-scale flows of energy and mass that characterise Earth's climate respond to increased atmospheric greenhouse gas concentrations?

Answering such questions has been a long-standing scientific challenge, largely because the scientific principles and tools required to understand and predict

[1] *Equilibrium* is used here in the thermodynamic sense, and not in the dynamic sense of stationarity.

non-equilibrium behaviour have been lacking. In many cases we may not know the underlying equations of motion exactly (especially the case in biology); with only the conservation laws (of energy, mass, momentum and/or charge) as guiding principles, there remains a large number of possible behaviours to choose from. Even when the underlying equations of motion are known (more or less) exactly—for example, the Navier–Stokes equation of fluid mechanics[2]—computational limitations may restrict our ability to solve them. One response to this challenge is to exploit the fact that the macroscopic behaviour of complex, non-equilibrium systems represents the emergent outcome of a large number of microscopic degrees of freedom. Some of those underlying degrees of freedom may behave as 'noise' that averages out at macroscopic scales. This offers the possibility of predicting the emergent macroscopic behaviour from the laws of thermodynamics. We might then hope to understand the behaviour of non-equilibrium systems statistically, in terms of the average, collective behaviour of a large number of individual degrees of freedom. Here again, however, traditional thermodynamics gives us little to go on.

The First Law of Thermodynamics only gives us energy conservation, while the Second Law is qualitative—it tells us only the direction in which an isolated non-equilibrium system will evolve on the average: towards the state of equilibrium, in which the system's thermodynamic entropy adopts its largest value subject to any constraints on it. The Second Law thus implies that, on average, the total thermodynamic entropy $S_{tot} = S_{sys} + S_{env}$ of an isolated system consisting of an open non-equilibrium subsystem (sys) plus its environment (env) will not decrease (i.e. $dS_{tot}/dt \geq 0$). In particular, if the open subsystem is in a steady state (i.e. $dS_{sys}/dt = 0$), then on average the entropy of the environment (S_{env}) will not decrease (i.e. $dS_{env}/dt \geq 0$). As noted above, this behaviour is evident in the observed tendency of open systems to re-export energy and matter to their environment in a higher entropy form than that in which they receive it.

Crucially, however, the Second Law is mute on two counts. Firstly, it does not predict the actual value of dS_{tot}/dt (i.e. the average rate at which S_{tot} increases). Secondly, as the mathematical physicist James Clerk Maxwell was one of the first to appreciate [2], the Second Law is statistical in character, rather than being a dynamical law. It is a statement about the average behaviour of isolated systems. However, it does not tell us the probability of statistical fluctuations in energy and mass flow for which, at least momentarily and locally, $dS_{tot}/dt < 0$, as when (for example) a group of gas molecules happens to move collectively from a region of low concentration to a region of higher concentration. And yet knowing these quantities—the average rate of entropy increase, and the probability of entropy-decreasing fluctuations—is central to answering some of the fundamental and practical questions mentioned above. Beyond the Second Law, the behaviour of entropy production becomes a key focus of study.

[2] Strictly speaking, the Navier–Stokes equation is only approximate; the (linear) expression for the stress tensor is only valid close to equilibrium.

The aim of this introductory chapter is to orient and guide the reader of this book. We begin with a rapid flight over the landscape of non-equilibrium principles that have been proposed beyond the Second Law (Sect. 1.2). For now, that landscape is still forming; it remains a rather fragmented one and we highlight some of the challenges one encounters in trying to negotiate it (Sect. 1.3). The key challenge is to find connections within this landscape, to construct bridges between previously isolated islands. In Sect. 1.4 we highlight some of the connections suggested to us by the recent work presented in this volume. Summarizing these in Sect. 1.5, we offer a tentative road map of the current landscape, as well as possible directions for future research.

Given the current state of play, we attempt no more than a partial synthesis here—partial in both perspective and scope. Thus Sects. 1.4 and 1.5 present one particular view of this exciting area of science, and where it might go next. It does not represent a consensus view of the contributing chapter authors, as will be clear from the diversity of perspectives this book brings together. And even at that, it does not pretend to paint a complete picture. Nevertheless, we hope this tentative road map will encourage the reader to develop his or her own vision of the landscape beyond the Second Law, and of the most fruitful paths to explore within it.

1.2 Beyond the Second Law: The Search for New Principles

Our main aim here is to give a brief overview of the landscape of non-equilibrium principles that have been proposed beyond the Second Law. Discussion of the key challenges in negotiating this landscape (ambiguities of meaning etc.) is deferred to Sect. 1.3.

1.2.1 Paltridge's MaxEP, the Fluctuation Theorem …

Within the last few decades, significant progress has been made towards developing and applying new principles of thermodynamics for non-equilibrium systems that go beyond the Second Law. With regard to the average value of dS_{tot}/dt and the probability of entropy-decreasing fluctuations, two key concepts have emerged: respectively, the principle of Maximum Entropy Production (MaxEP) and the Fluctuation Theorem (FT).

MaxEP is often stated verbally as a sort of codicil to the Second Law, according to which it is asserted that an open system adopts the stationary state ($dS_{sys}/dt = 0$) in which $dS_{tot}/dt = dS_{env}/dt$ attains its largest value possible within the constraints acting on the system. That is, a stationary open subsystem plus its environment not only tends to equilibrium ($dS_{tot}/dt = dS_{env}/dt \geq 0$) but, it is claimed, does so as fast as possible (maximum dS_{env}/dt) subject to any constraints.

In the seminal work of Garth Paltridge [3–5] in the 1970s and 1980s, MaxEP was applied to simple steady-state energy balance models of Earth's climate. Maximizing the entropy production associated with material heat transport in the atmosphere and oceans produced realistic predictions of the stationary latitudinal profiles of surface temperature, cloud fraction and equator-to-pole material heat transport. Somewhat surprisingly, this success was achieved when the maximization was subject to the sole constraint[3] of global energy balance, in the absence of any dynamical information such as planetary rotation rate.

Paltridge's MaxEP principle selects one among several climate states compatible with global energy balance [3–6]. It is the archetype for analogous MaxEP principles constrained only by global mass balance that have been applied with similar success to other non-equilibrium selection problems (e.g. crystal growth morphology, macromolecular evolution, plant growth strategies) [7–13]. For brevity, in the following we will refer to these collectively as 'Paltridge's MaxEP'—i.e. MaxEP principles in which the key constraints are global energy and/or mass balance. Despite these successes, the theoretical basis for Paltridge's MaxEP has remained elusive and this has hampered its acceptance by the wider scientific community.

The Fluctuation Theorem (FT) [14–16] concerns the probabilities of trajectories and their time reverse in microscopic phase space. Roughly speaking, the FT states that the probability of observing an entropy change $-d$ relative to that of an entropy change $+d$ over a given time period is exponentially small in d. Since d is an extensive quantity in both space and time (i.e. the entropy change increases with both the size of the system and the time period), the FT implies that macroscopic decreases in entropy, although possible, are extremely rare. In contrast, we expect to see frequent entropy-decreasing fluctuations in small (e.g. nanoscale) systems observed over short periods. Significantly, the FT also implies the Second Law inequality, i.e. the ensemble average[4] of d is non-negative.

1.2.2 … and other Principles

Prior to Paltridge's MaxEP principle, several earlier non-equilibrium principles had also been proposed, involving entropy production or dissipation in one guise or another (see e.g. the excellent review in [13]). A selection of these are summarised in Table 1.1: they include Onsager's MaxEP principle [17, 18], Prigogine's minimum entropy production (MinEP) theorem [19], Kohler's MaxEP principle in statistical transport theory [20, 21], and Ziegler's MaxEP principle for

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3 However, Paltridge's energy balance model still contained a number of *ad hoc* assumptions and parameterizations (see Herbert and Paillard Chap. 9).

4 The ensemble average is over the probability distribution of microscopic trajectories in phase space (see Sect. 1.4.1).

Table 1.1 A fragmented landscape. A selection of different dissipation- and entropy-related variational principles $H(y|C)$, defined in terms of the function that is maximised (H), the variables being optimised (y), the constraints (C), and the key prediction. The table entries above and below the dashed line describe principles that are conjectured to apply, respectively, close to and far from equilibrium (linear and non-linear regimes). Σ_i denotes a sum over $i = 1, \ldots n$ (this may be generalised to continuous systems). Abbreviations: *EP* entropy production; *GCM* general circulation model; *KE* kinetic energy; *LBE* linearized Boltzmann equation; *RTE* radiative transport equation; *UBT* upper bound theory of fluid turbulence

Variational principle	Maximised function, H	Variables, y	Constraints, C	Key prediction
Onsager MaxEP [17, 18]	$\Sigma_i J_i X_i - 1/2\Sigma_{ij} R_{ij} J_i J_j$	Fluxes[1] $J_i (i = 1, \ldots n)$	Fixed forces: $X_i = X_i^* \ (i = 1, \ldots n)$	Linear flux-force relations: $J_i = \Sigma_j R_{ij}^{-1} X_j^*$
Prigogine MinEP [19]	$-\Sigma_{ij} R_{ij}^{-1} X_i X_j$	Free forces $X_i (i = k+1, \ldots n)$	Fixed forces: $X_i = X_i^* (i = 1, \ldots k)$; Linear flux-force: $X_i = \Sigma_j R_{ij} J_j$	$J_i = 0 \ (i = k+1, \ldots n)$
Kohler MaxEP (solution to LBE) [20, 21]	EP of molecular collisions $\sigma_{coll}(f)$ (source term in continuity equation for entropy $s = -\int f \ln f d\mathbf{v}$)	One-particle velocity ($\mathbf{v}$) distribution function $f(\mathbf{v})$	Fixed temperature and concentration fields; $\sigma_{coll}(f)$ = entropy export (steady-state condition)	Stationary $f(\mathbf{v})$ near equilibrium
- - - - -	- - - - -	- - - - -	- - - - -	- - - - -
Radiative MinEP (solution to RTE) (Chap. 12)	$-\sigma_{tot}(I_v)$, where $\sigma_{tot}(I_v)$ = total (radiation + matter) EP	Radiation intensity, I_v	Various moment constraints on I_v	Radiation transport coefficients
Ziegler MaxEP [22]	Dissipation $\sigma(J)$ (assumed to be a known function of the fluxes J_i)	Fluxes[1] $J_i (i = 1, \ldots n)$	Fixed forces: $X_i = X_i^* \ (i = 1, \ldots n)$; $\sigma(J) = \Sigma_i J_i X_i^*$	Non-linear flux-force relations: $X_i^* \propto \partial\sigma(J)/\partial J_i$ (orthogonality)
Paltridge MaxEP [3–13]	Various EP-related functions of the form $\Sigma_i J_i X_i$	J_i and $X_i (i = 1, \ldots n)$	Steady-state energy/mass balance (neither X_i nor J_i need be fixed)	Stationary J_i and X_i (non-linear regime)

(continued)

Table 1.1 (continued)

Variational principle	Maximised function, H	Variables, y	Constraints, C	Key prediction
Malkus UBT [23–28]	Various dissipation-related functions of turbulent flow (including KE dissipation)	Mean velocity field	A restricted set of spatial integrals of the Navier–Stokes equation	Mean stationary velocity field (non-linear regime)
Max KE dissipation [29]	Dissipation of KE in a GCM	GCM parameters	Steady-state GCM dynamics	Dynamical climate features
Boltzmann-Gibbs-Jaynes MaxEnt [30–34]	Relative entropy $-\Sigma_i p_i \ln(p_i/q_i)$	Posterior probability of outcome i, p_i	Available or relevant information: $\Sigma_i p_i f_{ik} = F_k (k = 1, \ldots m)$; Prior probability q_i of outcome i	Most likely sampling distribution p_i

[1] The Onsager and Ziegler MaxEP principles can also be formulated in the space of forces $(y = X)$ subject to fixed fluxes $(J = J^*)$

dissipative materials [22]. Also, starting in the 1950s, several variational principles for fluid turbulence were developed by Malkus and others, based on maximising various dissipation-like functions of the flow [23–28]—an approach known as the Upper Bound Theory (UBT) of fluid turbulence. Table 1.1 also includes three other variational principles: a variant of Kohler's principle applied to radiative transport, in which entropy production is minimized rather than maximized (Christen and Kassubek Chap. 12); a principle of maximum kinetic energy (KE) dissipation, suggested by recent climate simulations using a General Circulation Model (GCM) [29], which is also one of the principles emerging from UBT; and the Boltzmann-Gibbs-Jaynes Maximum Entropy (MaxEnt) algorithm [30–34].

Anticipating the discussion in Sect. 1.3, the landscape presented by these principles is a fragmented one. In order to compare and contrast the elements of this landscape, Table 1.1 describes each principle in terms of the dissipation- or entropy-related function H that is maximized, the variables (y) being optimised, and the constraints (C). Key predictions of each principle are given in the last column.

1.2.2.1 Onsager's MaxEP, Prigogine's MinEP

Onsager's original motivation was to establish a theoretical framework for the development of near-equilibrium thermodynamics [17, 18]. Specifically, Onsager's MaxEP principle may be used to derive the near-equilibrium, linear 'constitutive relations' between generalised thermodynamic fluxes J_i and forces X_i, i.e. $J_i = \Sigma_j L_{ij} X_j$ (generalisations of the laws of Fick and Ohm, for example), where the matrix of coupling coefficients[5] is symmetric (i.e. $L_{ij} = L_{ji}$, also known as reciprocity). Prigogine's principle [19] assumes linear flux-force relations as a starting point, and some of the forces are then relaxed: it describes the behaviour of the entropy production, given by $\Sigma_{ij} L_{ij} X_i X_j$, 'when we let go of some of the leads' [21].

1.2.2.2 Kohler's MaxEP, Radiative MinEP

In a separate context, Kohler [20] established a mathematical variational principle to solve the linearised Boltzmann equation (LBE) describing the statistical transport properties of a rarified gas. Subsequently, Ziman [21] recast the Boltzmann equation in the language of thermodynamic fluxes and forces and showed Kohler's principle to be mathematically equivalent to Onsager's MaxEP principle. This suggested to Ziman that Kohler's principle was not just a convenient mathematical trick but had the following physical interpretation: the entropy production of molecular collisions is maximized subject to fixed thermodynamic forces (e.g. temperature and concentration fields), and to the steady-state condition

[5] Here L_{ij} is the inverse of the matrix R_{ij} in Table 1.1.

that the internal entropy production is balanced by dissipation of heat into the environment.

For the problem of radiative transfer in gases or plasmas, the relevant principle appears to be one of MinEP rather than MaxEP (Christen and Kassubek, Chap. 12 and references therein; see also Niven and Noack, Chap. 7). Moreover, when the radiative transfer equation is considered as a LBE, the linearisation is exact because photons do not interact with each other, so that the solution is valid for radiation that is arbitrarily far from thermal equilibrium.

1.2.2.3 Ziegler's MaxEP

The original motivation behind Ziegler's MaxEP principle [22] was to derive the non-linear constitutive relation between generalised forces X_i and fluxes J_i (e.g. stress–strain relations) in dissipative materials far from equilibrium. What are the fluxes given the forces (and vice versa)? As Table 1.1 indicates, the key prediction of Ziegler's MaxEP (subject to fixed generalised forces $X_i = X_i^*$ and the constraint $\sigma(J) = \Sigma_i J_i X_i^*$) is a constitutive relation that satisfies an orthogonality condition (OC), according to which the generalised force X^* (considered as a vector with components X_i^*) lies in the direction normal to the contours of $\sigma(J)$ in flux space.[6] Ziegler originally derived the OC using a geometrical argument, based on the assumption that the vector X can be derived solely from properties of the scalar dissipation function $\sigma(J)$; the existence and nature of the function $\sigma(J)$ were also assumptions (Houlsby, Chap. 4).

Ziegler noted the equivalence of the OC to a variational principle (Ziegler's MaxEP)—i.e. maximizing $\sigma(J)$ with respect to J under the constraints in Table 1.1—as a possibly more general thermodynamic basis for the OC. And yet a fundamental basis for the assumptions underlying either derivation of Ziegler's OC (geometrical or variational) has yet to be established; moreover, a direct experimental test of the OC has yet to be derived [35]. In practice, therefore, the OC has been adopted as a working hypothesis for classifying different theoretical behaviours of dissipative materials.

1.2.2.4 Upper Bound Theory of Fluid Turbulence, Maximum KE Dissipation

The UBT of fluid turbulence was developed by Malkus and others [23–28] to predict the mean turbulent velocity field, by maximizing various dissipation-related functionals of the flow. Initially these took the form of maximum transport principles (maximum heat flow, maximum momentum transport) [23–25, 27].

[6] An equivalent orthogonality condition for the direction of the generalised fluxes J in force space can be stated in terms of the contours of $\sigma(X)$.

Later, Kerswell [26] analysed a more general family of functionals related to KE dissipation by the mean and fluctuating components of the flow. Maximum KE dissipation by the mean flow was also proposed more recently by Malkus [28].

Crucially, the maximization was subject to a restricted number of dynamical constraints, obtained as integral properties of the Navier-Stokes equation (e.g. global power balance and horizontal mean momentum balance within a horizontally sheared fluid layer) rather than the full dynamics. The UBT is thus analogous in spirit to Paltridge's MaxEP: i.e. select one of many possible stationary states compatible with a restricted number of constraints representing the relevant physics on macroscopic scales, the rest being treated as 'noise'. However, one key difference is that UBT includes some dynamical information (momentum balance) in addition to global energy balance; another key difference is in the nature of the extremized function (e.g. viscous dissipation of KE [28] rather than thermal dissipation [3–6]).

Intriguingly, simulations using the FAMOUS GCM [29] also showed that key dynamical features of Earth's climate were close to a maximum of KE dissipation (Table 1.1).

1.2.2.5 Boltzmann-Gibbs-Jaynes Maximum Entropy

Finally we have the Boltzmann-Gibbs-Jaynes principle of Maximum Entropy (MaxEnt) [30–34]. This principle stands somewhat apart from the others in Table 1.1, both conceptually and in practice (see Dewar and Maritan, Chap. 3; Niven and Noack, Chap. 7). MaxEnt predicts a probability distribution p_i over microscopic outomes i, from which macroscopic quantities may be predicted as averages over p_i. The maximized function H is the relative entropy (or negative Kullback–Leibler divergence) of p_i and a prior distribution q_i; H reduces to the Shannon entropy when q_i is uniform. The maximization is subject to constraints on certain moments of p_i (representing available or relevant physical information), as well as the specified prior probabilities q_i. MaxEnt has several interpretations (Chaps. 3 and 7, and references therein). One fairly concrete interpretation of the MaxEnt distribution is that it corresponds to the most likely frequency distribution of outcomes that would be observed in a long sequence of independent observations of a system that is subject to the given constraints; MaxEnt also has an information-theoretical interpretation as the 'least-informative' p_i [32, 33].

MaxEnt has a long history, starting with Boltzmann's discovery that MaxEnt expresses the asymptotic behaviour of multinomial probabilities [30], and the early development of equilibrium statistical mechanics by Gibbs [31]. The later reappearance of $-\Sigma_i p_i \ln p_i$ (Shannon entropy) in the development of information theory [36, 37], as a measure of missing information, led Jaynes to see MaxEnt as a general method of statistical inference from incomplete information [32, 33]. In view of its general nature, Jaynes promoted MaxEnt as a theoretical framework for non-equilibrium as well as equilibrium statistical mechanics. When applied to non-equilibrium systems, MaxEnt leads to non-linear flux-force relationships that automatically satisfy Onsager reciprocity and reduce to linear form in the near-equilibrium limit [38–40]. Although MaxEnt provides a foundation for equilibrium and non-equilibrium thermodynamics, its physical interpretation remains a subject of debate (e.g. [41]) that has, like Paltridge's MaxEP, hampered its wider acceptance.

1.3 A Fragmented Landscape

After this rapid tour, the student would be forgiven for being confused by the sheer number and variety of entropy production-related principles, as well as by the diverse ways in which they have been applied to non-equilibrium systems. One sees a fragmented landscape of principles and applications, and faces three key difficulties in negotiating it.

1.3.1 Different Histories

One difficulty is historical: the above theoretical principles (Table 1.1) were developed at different times, more or less independently of one other. Some theoretical links between the earlier variational principles (Onsager, Prigogine, Ziegler) have been identified [13]. For example, Ziegler's MaxEP principle reduces to Onsager's in the near-equilibrium limit, while Prigogine's is a corollary of Onsager's that involves additional constraints. However, the links (if any) between Paltridge's MaxEP, the Fluctuation Theorem, Kohler's MaxEP, radiative MinEP, UBT, maximum KE dissipation and MaxEnt (and between these and Ziegler's principle) have remained obscure.

1.3.2 Different Meanings

A second difficulty, and one that compounds the first, is semantic. The terms *entropy production* or *dissipation* are defined and used by different workers in different ways, creating ample room for confusion. Some approaches take entropy production as a given function of thermodynamic fluxes and forces [3–9, 11, 12, 17–19, 22–28], while others define entropy production from an underlying microscopic picture [10, 14–16, 21, 42, 43]. Moreover it does not help that Onsager called his MaxEP principle 'least dissipation of energy', or that Paltridge originally called his principle 'minimum entropy exchange' before resorting to MaxEP!

Yet further scope for confusion arises in the context of extremal principles. For example, from the name alone one might conclude that Paltridge's MaxEP principle contradicts Prigogine's principle of MinEP, whereas these two extremal principles refer to quite different situations. Paltridge's MaxEP principle (e.g. as applied to climate systems [3–6]) is a selection principle between different far-from-equilibrium stationary states. In contrast, Prigogine's principle describes the non-stationary behaviour of the entropy production of near-equilibrium systems[7] when a subset of the thermodynamic force constraints is relaxed; it says only that the unique stationary state has lower entropy production than any non-stationary state, and does not provide a selection principle in situations where there are multiple stationary states (for a further critique of Prigogine's MinEP, see [44]).

To have any chance of making sense of the landscape, one must look beyond the semantics and identify three key aspects (Table 1.1) of each extremal principle, which we denote by $H(y|C)$: (1) which entropy production or dissipation function (H) is being maximised? (2) with respect to which variable(s) (y)? and (3) subject to which constraint(s) (C)? Unless extremal principles are clearly stated in this way, the potential for confusing apples with pears is essentially infinite.

1.3.3 Lack of Foundations

A third related difficulty in negotiating the current landscape lies in the somewhat *ad hoc* way in which, for example, Paltridge's MaxEP has been applied in practice, with many aspects open to ambiguity. Which entropy production function (H) is to be maximised? In some discussions of the physical interpretation of H, the system entropy $S_{sys} = \int s_{sys} dV$ ($V =$ system volume) is treated as a physical quantity obeying a local continuity equation ($\partial s_{sys}/\partial t = -\nabla \cdot \boldsymbol{j_s} + \sigma$ with entropy flux $\boldsymbol{j_s}$ and local entropy production rate σ). In a stationary state all the entropy production $\int \sigma dV (\geq 0)$ within the system is exported to the environment, and by MaxEP is then meant maximum $\int \sigma dV$. However, missing from this interpretation of MaxEP is a clear definition of σ itself! In the definition of σ for flow systems, Niven and Noack (Chap. 7) also reveal some fundamental problems related to decomposition of the flow into mean and fluctuating parts (the entropy production closure problem).

Thus it was only through a process of trial and error that Paltridge [3] stumbled upon maximisation of the entropy production associated with thermal dissipation by the equator-to-pole heat transport in the oceans and atmosphere,[8] rather than the global entropy production associated with short- and long-wave radiative exchange at the top of the atmosphere. In contrast, as noted above, simulations

[7] The regime of linear force-flux relations.

[8] In Paltridge's zonally-averaged climate model [4], thermal dissipation is given by $\sigma = \Sigma_i J_i X_i$ where $J_i =$ material heat transport between meridional zones i and $i + 1$, and $X_i = 1/T_{i+1} - 1/T_i$ is the corresponding inverse temperature difference.

using the FAMOUS GCM [29] showed that key dynamical climate features were close to a maximum of KE dissipation rather than thermal dissipation.

A similar ambiguity about the choice of dissipation function to maximise afflicts the UBT in fluid turbulence; for example, from among a general family of dissipation functionals Kerswell [26] was unable to identify a universal one whose maximization applies to all flow problems. In all of these cases, the main source of ambiguity in the choice of extremized function is the lack of a rigorous theoretical foundation for Paltridge's MaxEP and the UBT. The theoretical basis of Kohler's MaxEP is on firmer ground, as it may be proved as the mathematical solution to the linearized Boltzmann equation [13, 20, 21]. Overall, however, what is lacking is a selection principle for selection principles!

The debate on the theoretical basis of MaxEP extends to whether MaxEP is even a physical principle at all [e.g. 13, 41]. Another source of ambiguity lies in the choice of appropriate constraints, a limitation that applies also to MaxEnt. Moreover, by its very nature as a generic inference algorithm, applications of MaxEnt also require a choice to be made for the set of outcomes i whose probabilities p_i are to be predicted (Table 1.1); i may represent microscopic paths in phase space, macroscopic fluxes defined within the system and/or on its boundary, or indeed any quantity of which we have incomplete information (see Chaps. 3 and 7, and references therein).

Finally, so far we have been referring to near-equilibrium and far-from-equilibrium principles (Table 1.1) when we have not defined what we mean by distance from equilibrium. If by near-equilibrium systems we mean systems obeying linear constitutive relations (Table 1.1 and footnote 7), then the definition is circular. Of course, entropy production itself is a measure of distance from equilibrium (since it vanishes in equilibrium) but, as we have seen, there are many definitions of entropy production!

1.4 Making Connections

Here we try to pull together some of the common threads running through this book, with entropy production playing a key unifying role. An attempt will be made to synthesise these connections in Sect. 1.5. In anticipation, the reader is referred to the tentative road map shown in Fig. 1.1.

1.4.1 The Fluctuation Theorem, MaxEnt, and a Generic MaxEP Principle

We have seen that the plethora of non-equilibrium extremal principles in Table 1.1 involve various definitions of entropy production and dissipation. Is there a

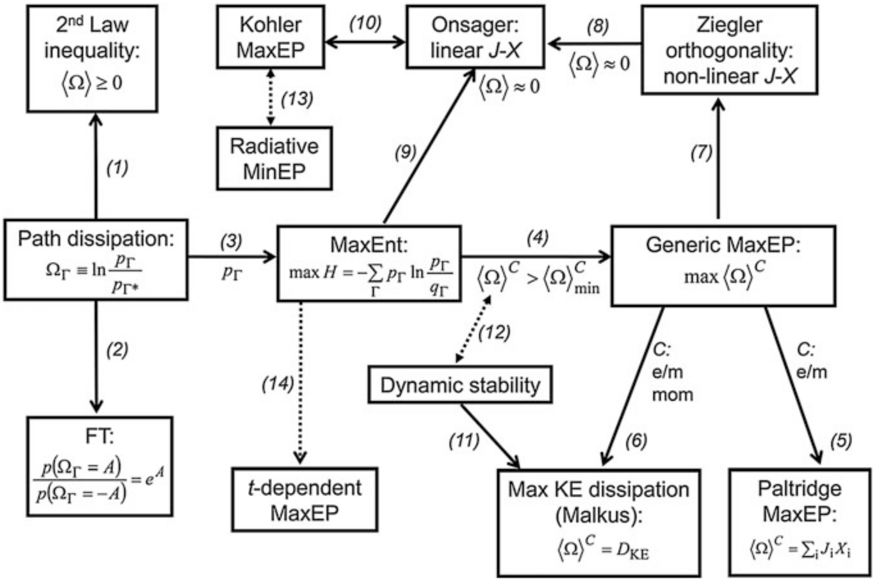

Fig. 1.1 The Second Law and beyond: a tentative road map of theoretical links (*solid arrows*, roads *1–11*) and future research directions (*dashed arrows*, roads *12–14*). See text for notation

fundamental entropy production- or dissipation-like quantity on which we can build a more coherent picture? Here we suggest there is, defined at the level of microscopic trajectories in phase space, a definition that links the Fluctuation Theorem, MaxEnt and MaxEP.

Specifically, let p_Γ denote the probability that the system follows microscopic trajectory (or path) Γ in phase space,[9] and let Γ^* denote the time-reverse of Γ. In equilibrium we expect that $p_\Gamma = p_{\Gamma^*}$ (no net fluxes on average); however, when a system is driven out of equilibrium by an external force (e.g. non-uniform heating on the boundary), the odds are changed in favour of a particular average flow direction, and then we expect that $p_\Gamma \neq p_{\Gamma^*}$. The trajectory-dependent quantity Ω_Γ (called the *dissipation function* in Reid et al., Chap. 2) defined by

$$\Omega_\Gamma = \ln \frac{p_\Gamma}{p_{\Gamma^*}} \quad (1.1)$$

emerges as a central concept in both the Fluctuation Theorem (Reid et al., Chap. 2) and a proposed generic MaxEP principle derived from MaxEnt (Dewar and

[9] The notation is simplified here for clarity. In terms of the notation of Chap. 2, for example, $p_\Gamma = p(\mathbf{\Gamma}(0), 0)$ is the probability of observing the system in an infinitesimal region around $\mathbf{\Gamma}(0)$ at time $t = 0$, where $\mathbf{\Gamma}(t)$ denotes the phase space vector at time t, and $p_{\Gamma^*} = p(\mathbf{\Gamma}^*(\tau), 0)$ where $\mathbf{\Gamma}^*(\tau)$ is obtained from $\mathbf{\Gamma}(\tau)$ by reversing all the particle velocities.

Maritan, Chap. 3). Two key results follow as mathematical consequences of the above definition[10]:

$$\frac{p(\Omega_\Gamma = A)}{p(\Omega_\Gamma = -A)} = e^A \tag{1.2}$$

and

$$\langle\Omega\rangle = \sum\nolimits_\Gamma p_\Gamma \ln\frac{p_\Gamma}{p_{\Gamma*}} \geq 0, \tag{1.3}$$

with equality if and only if $p_\Gamma = p_{\Gamma*}$; the sum in Eq. (1.3) extends over all microscopic trajectories (i.e. it includes both Γ and Γ*). Equation (1.2) is the Fluctuation Theorem; it implies that trajectories with negative Ω_Γ are exponentially less likely to be observed than trajectories with positive Ω_Γ. In Eq. (1.3), $\langle\Omega\rangle$ is the Kullback-Leibler divergence of p_Γ and $p_{\Gamma*}$; it is a measure of how different p_Γ and $p_{\Gamma*}$ are. In other words, $\langle\Omega\rangle$ is a measure of time-reversal symmetry breaking (or *irreversibility* in the language of Chap. 3)—and therein lies its fundamental character, as well as the key to its eventual physical interpretation as a thermodynamic entropy production. Equation (1.3) states that the average value of Ω_Γ is non-negative; this result, known as the Second Law inequality, is a mathematical consequence of Gibbs' inequality. The value $\langle\Omega\rangle = 0$ (i.e. $p_\Gamma = p_{\Gamma*}$) corresponds to thermodynamic equilibrium, underpinning the interpretation of $\langle\Omega\rangle$ as a measure of distance from equilibrium.

Clearly, the physical consequences of these purely mathematical results can only emerge when some additional physical information is built into p_Γ. In Chap. 2, this is done by deriving p_Γ from a microscopic model of the underlying molecular dynamics. In Chap. 3, p_Γ is derived[11] from MaxEnt constrained by a restricted subset of the underlying dynamics, representing those key aspects of the dynamics that are known (or assumed) to be relevant on macroscopic scales. Equation (1.3) is also consistent (up to a factor 2) with the definition of entropy production that emerges from the MaxEnt analysis of flow systems in Chap. 7, in which constraints on various mean flow rates are imposed.

In each case, whether p_Γ (or $p(\boldsymbol{f})$, see footnote 11) is derived from molecular dynamics (Chap. 2) or macroscopic flux constraints (Chaps. 3 and 7), $\langle\Omega\rangle$ may be interpreted physically as a *generalised entropy production*, defined for systems arbitrarily far from equilibrium. The FT and Second Law inequality then become statements about physically-meaningful dissipation-like quantities. The generic

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[10] If $\delta(i,j)$ denotes the Kronecker delta function [0 if $i \neq j$, 1 if $i = j$], Eq. (1.2) follows from $p(\Omega_\Gamma = A) = \Sigma_\Gamma p_\Gamma \delta(\Omega_\Gamma, A)$ = [change of variable] $\Sigma_\Gamma p_{\Gamma*} \delta(\Omega_{\Gamma*}, A)$ = (from Eq. 1.1) $\Sigma_\Gamma p_\Gamma \exp(-\Omega_\Gamma)\delta(-\Omega_\Gamma, A) = e^A \Sigma_\Gamma p_\Gamma \delta(\Omega_\Gamma, -A) = e^A p(\Omega_\Gamma = -A)$. Equation (1.3) follows from Gibbs' inequality: $-\Sigma_i p_i \ln p_i \leq -\Sigma_i p_i \ln q_i$ for any probability distributions p_i and q_i, with equality if and only if $p_i = q_i$ for all i.

[11] In Chap. 3, MaxEnt is used to construct $p(\boldsymbol{f})$, the probability distribution of macroscopic fluxes $\boldsymbol{f}$, rather than p_Γ; the formalism can be re-expressed in terms of p_Γ as shown in [42].

MaxEP principle derived from the MaxEnt argument given in Chap. 3 then supplements the Second Law inequality with the statement that not only is $\langle\Omega\rangle$ non-negative but $\langle\Omega\rangle$ takes on its maximum value attainable under the imposed constraints.[12]

1.4.2 Which Entropy Production is Extremised? An Emerging Pattern

The majority of applications described in Part III of this book pertain to MaxEP and its variants. In the absence of an accepted theoretical basis for MaxEP, a pragmatic approach has seemed to be the only way forward. By applying MaxEP in many different ways, using different candidate entropy production functions, and seeing in which situations it appears to work in practice, one might gain insights into its theoretical basis.

Using simple energy balance models (EBMs) that avoid some of the *ad hoc* assumptions and parameterizations of Paltridge's EBM [3–5], Herbert and Paillard (Chap. 9) and Fukumura and Ozawa (Chap. 11) provide further evidence that the broad *thermal* characteristics of some planetary climates (e.g. latitudinal profiles of surface temperature and meridional heat flows) may be reproduced with reasonable accuracy by maximizing the thermal entropy production associated with the material transport of heat across temperature gradients, subject only to the constraint of global energy balance. These results do not invoke any dynamical constraints, but are nevertheless conditional on there being sufficient mass to sustain advective heat transport (Chap. 11), a conclusion also reached in [45]. Subject to this proviso, the implication then is that fluids with different dynamical properties (e.g. different viscosities), but subject to the same global energy balance constraint, will self-organize their velocity fields to achieve the same overall optimal pattern of heat flow.

In contrast, in order to predict dynamical characteristics that depend explicitly on the *velocity field* (including the velocity field itself), a principle of maximum KE dissipation appears to take precedence. In climatology, this result is suggested by a dynamic sensitivity analysis of FAMOUS, a GCM of intermediate complexity [29]; in horizontal shear turbulence, maximum KE dissipation also accurately reproduces the mean velocity profile over a large range of forcing conditions [28]; the same principle also emerges as an accurate predictor of the steady orientation of a body settling in a viscous fluid (Vaidya, Chap. 13). Yet another principle, maximum heat flow, appears to govern the stability of stationary convective states

[12] Specifically (see Chap. 3), when the non-equilibrium driving force is such that $\langle\Omega\rangle^C > \langle\Omega\rangle^C_{min}$, then MaxEnt implies $\langle\Omega\rangle = \langle\Omega\rangle_{max}$. Here C denotes a restricted set of stationarity constraints, the nature of which determines the physical nature of $\langle\Omega\rangle^C$ as an entropy production or dissipation functional; $\langle\Omega\rangle^C_{min}$ and $\langle\Omega\rangle^C_{max}$ are the lower and upper bounds on $\langle\Omega\rangle^C$.

in lattice-Boltzmann simulations of Rayleigh-Bénard convection (Weaver et al., Chap. 14); under fixed-temperature boundary conditions this is equivalent to maximum thermal entropy production.

From this pragmatic approach, therefore, the empirical and numerical evidence appears to suggest that there is no universal entropy production functional that is maximized in all problems. However, from a variety of different applications two key principles have emerged—maximum thermal dissipation and maximum KE dissipation—as a guide to constructing a more fundamental theory. One would like such a theory to tell us a *priori* which functional to maximize. What insights do existing theoretical approaches provide? For example, can we unify at least some of the extremal functions in Table 1.1 in terms of the generalised entropy production $\langle \Omega \rangle$ discussed in Sect. 1.4.1?

1.4.3 MaxEP and Dynamic Stability: Emerging Theories

Several chapters in the theoretical section of this book (Part II), and studies elsewhere, suggest that MaxEP and dynamic stability are closely related. For example, Kleidon et al. (Chap. 8) propose a maximum power principle (equivalent to maximum KE dissipation) for the selection of different flow structures in a simple model of Earth system KE; they use a heuristic dynamical stability argument to suggest that stationary states of maximum KE dissipation are preferred because they are the most stable. Ozawa and Shimokawa (Chap. 6) come to a similar conclusion by deriving a necessary condition for the local KE dissipation rate of a convective fluid to increase over time. In an earlier study, Malkus [28] derived maximum global KE dissipation by the mean flow as a necessary condition for the stability of stationary states in horizontal shear turbulence.

Further numerical evidence that MaxEP and dynamic stability are intimately linked emerges from the stability analysis of crystal growth morphologies (Martyushev, Chap. 20), which shows that the coexistence of two growth morphologies occurs when their respective entropy productions (defined in terms of the local velocity of the crystal surface) are equal. Simulations of Rayleigh-Bénard convection (Weaver et al., Chap. 14) indicate that stationary convective states of maximum heat transport are the most stable (cf. [25]).

A common feature of the analyses linking dynamical stability to maximum KE dissipation is their incorporation of momentum balance[13] as a constraint, in addition to the global energy balance constraint under which Paltridge maximized thermal dissipation. This suggests that there might be a link between the choice of extremized function and the choice of constraints, and, further, that dynamical stability underlies that link.

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[13] In Chap. 8 and [28], only a spatially-averaged momentum balance constraint is imposed, rather than the full Navier–Stokes equation.

Dewar and Maritan (Chap. 3) propose such a connection, based on the application of MaxEnt to non-equilibrium systems under generic dynamical constraints. Here, the physical nature of the generalised entropy production $\langle\Omega\rangle$ indeed depends on the choice of constraints. Specifically, when only global energy (or mass) balance is imposed, MaxEnt predicts that $\langle\Omega\rangle$ is the entropy production by heat (or mass) flow, consistent with the extremised function in Paltridge's MaxEP. In horizontal shear turbulence, when the additional (spatially-averaged) momentum constraint of Malkus [28] is imposed, MaxEnt predicts that $\langle\Omega\rangle$ is KE dissipation by the mean flow, consistent with [28]. Moreover, dynamical stability plays a crucial role here: when the non-equilibrium driving force is sufficient to make the stationary state of minimum $\langle\Omega\rangle$ dynamically unstable (see footnote 12 and Chap. 3), MaxEnt predicts that $\langle\Omega\rangle$ adopts its maximum value.

The suggestion here is that there may indeed exist a universal entropy production functional that is maximized in all problems—in the form of $\langle\Omega\rangle$ defined by Eq. (1.3)—but that $\langle\Omega\rangle$ manifests itself as thermodynamic entropy production in different ways (e.g. thermal dissipation, KE dissipation) according to the constraints on the system. We might think of this as the result of different constraints confining the dissipation of free energy to different degrees of freedom, as described by different thermodynamic dissipation functions.

1.4.4 MaxEnt and Ziegler's MaxEP

What is the link, if any, between Ziegler's MaxEP and the other extremal principles in Table 1.1? As we noted in Sect. 1.2, Ziegler's MaxEP lacks a rigorous theoretical basis. Given the proposed argument for a MaxEnt basis of MaxEP as a generic stationary state selection principle (Chap. 3), it is natural to examine whether MaxEnt might also provide a basis for Ziegler's MaxEP (or equivalently Ziegler's orthogonality condition, see Table 1.1).

Such a link was established in [43] for systems close to equilibrium.[14] Specifically, under fixed mean fluxes J_i^*, MaxEnt yields an orthogonality condition between the associated Lagrange multipliers λ_i and J_i^*, i.e. $J_i^* \propto \partial\sigma(\lambda)/\partial\lambda_i$. Here $\sigma(\lambda) = \langle\Omega\rangle$ is the dissipation function defined by Eq. (1.3), which according to MaxEnt can be expressed as a function of either J^* or λ. Equivalently, we can consider λ^* as given and derive the orthogonality condition $\lambda_i^* \propto \partial\sigma(J)/\partial J_i$. If we then identify λ_i with the thermodynamic 'force' conjugate to J_i, these results are identical to Ziegler's orthogonality condition in, respectively, X-space and J-space (Table 1.1). Whereas Ziegler's MaxEP assumes the functional form of $\sigma(J)$ a priori, this emerges from MaxEnt a posteriori.

Thus, close to equilibrium, Ziegler's orthogonality condition (OC) characterises the MaxEnt relation between flux constraints and their Lagrange multipliers. The fact

[14] The restriction of the analysis in [43] to near-equilibrium systems was pointed out in [46, 47].

that Ziegler's OC can also be derived from a separate maximization principle (Ziegler's MaxEP principle, Table 1.1) may perhaps be a 'red herring' for two reasons. Firstly, it is known that the generic relation between MaxEnt Lagrange multipliers and constraints can be solved mathematically as a variational principle [48]. Secondly, the max/min character of Ziegler's OC depends on the nature of the auxilliary constraints on λ; for example, $\sigma(\lambda)$ has a minimum with respect to variations in λ restricted to the plane $\Sigma_i \lambda_i J_i^* =$ constant (cf. Ziegler's MaxEP, Table 1.1). Applications to dissipative materials and land-atmosphere energy exchange are discussed, respectively, by Houlsby (Chap. 4) and Wang et al. (Chap. 16).

The equivalence of Ziegler's MaxEP and MaxEnt subject to given fluxes J^* is also apparent in the fact that both lead to linear flux-force relations close to equilibrium [13, 38–40] (see also Seleznev and Martyushev, Chap. 5). Moreover, the equivalence may be more general: in the derivation of a generic MaxEP principle from MaxEnt (Dewar and Maritan, Chap. 3), Ziegler's OC emerges as a property of MaxEP stationary states arbitrarily far from equilibrium.

1.4.5 The Physical Interpretation of MaxEP

The suggestion, then, is that MaxEnt offers a common theoretical framework that links at least some of the non-equilibrium extremal principles[15] in Table 1.1 (see also Fig. 1.1). If this is correct, the question of the physical significance of MaxEP (Paltridge, UBT, Ziegler …) boils down to that of MaxEnt itself.

Mathematically, MaxEnt is an algorithm that constructs a probability distribution p_i over some set of outcomes i subject to given constraints C (usually a restricted subset of the full underlying dynamics). The MaxEnt probability distribution p_i coincides with the most likely frequency distribution of outcomes that would be observed in an infinitely long sequence of independent samples, provided we have correctly identified the relevant constraints C that apply during the experiment (see Chap. 3 and references therein; also Chap. 7).

This implies that MaxEnt (hence MaxEP) can be used to answer two complementary questions: Given the constraints, what is the most likely system behaviour? Or, given the observed system behaviour, what are the key constraints governing it? Therefore we can use MaxEP in two ways—as a statistical selection principle or a method for inferring the relevant constraints—depending on which question we are asking. The latter question is less straightforward to answer than the former. It requires a trial and error approach in which by comparing MaxEnt predictions and observations we eventually home in on the relevant constraints (which usually comprise some restricted subset of the full dynamics, e.g. global energy balance, global momentum balance). In the former we can interpret

[15] For an alternative perspective, see Chap. 5.

MaxEnt as a physical (statistical) selection principle, just as we do the Second Law.

While it may be tempting to interpret MaxEP as a dynamical principle that reflects the evolution of a system towards the most stable stationary state (as suggested in Sect. 1.4.3), we should recall Maxwell's insight that the Second Law is statistical in nature, and not a dynamical principle [2]. Likewise, it may be more insightful to interpret stability arguments for MaxEP, based on a restricted subset of the full dynamics, in a statistical sense, as describing the most likely behaviour under those constraints.

Haff (Chap. 21) discusses the interplay between MaxEP and constraints in the context of biological and technological evolution. Evolutionary 'hang-ups' [49] may be short-term internal constraints that reflect slow degrees of freedom (e.g. the long abiotic phase of Earth's evolution, or the energy that is temporarily stranded in fossil fuels). Some of those constraints may relax over longer timescales. Thus, while predicting the current evolutionary state may not be straightforward, MaxEP may more readily tell us where evolution is heading once only a few easily-identifiable external constraints remain (e.g. global energy or mass balance). Dobovišek et al. (Chap. 19) investigate the extent to which the evolution of enzyme kinetics accords with MaxEP and MaxEnt constrained by mass balance. Lineweaver (Chap. 22) explores the question of how MaxEP may relate to the rate of evolution of the universe towards a state of thermodynamic equilibrium.

1.5 Towards a Synthesis

Figure 1.1 depicts a tentative road map of the theoretical links (solid arrows, roads *1-11*) suggested in Sect. 1.4, and in addition some directions for future research (dashed arrows, roads *12-14*). We emphasise again that this particular view of the landscape beyond the Second Law is a partial one, based mainly on the material presented in Chaps. 2–4, 6, 8, 9, 11–13, 18 and 19. Section 1.5.2 highlights some of the viewpoints and issues not featured in Fig. 1.1.

1.5.1 A Tentative Road Map

As indicated by roads *1-3*, the path probability p_Γ and path dissipation function Ω_Γ (Reid et al., Chap. 2) play a unifying role by linking the Second Law inequality, the Fluctuation Theorem (FT) and Maximum Entropy (MaxEnt). Road *4* links MaxEnt to a generic MaxEP principle (Dewar and Maritan, Chap. 3), in which the path relative entropy ($H = -\Sigma_\Gamma p_\Gamma \ln p_\Gamma / q_\Gamma$) is maximized with respect to p_Γ, subject to a restricted set of stationarity constraints (C) together with the criterion that the state of minimum dissipation is dynamically unstable, $\langle\Omega\rangle^{\mathrm{C}} > \langle\Omega\rangle^{\mathrm{C}}_{\min}$. As indicated by the superscript, the physical nature of the dissipation function $\langle\Omega\rangle^{\mathrm{C}}$

(i.e. its interpretation as a thermodynamic entropy production) depends on the nature of C. MaxEnt implies MaxEP, i.e. $\langle\Omega\rangle^{C}$ is maximized with respect to the stationary states compatible with C. When C represents global energy and/or mass balance (e/m, road *5*), we recover Paltridge's MaxEP (cf. Chaps. 9, 11, 19) in which $\langle\Omega\rangle^{C}$ takes the form of flux times force (e.g. heat flux times inverse temperature gradient; or mass flux times chemical affinity). When C includes global power balance *and* a spatially-averaged momentum balance constraint in horizontal shear turbulence [28] (e/m, mom, road *6*), we recover maximum KE dissipation (cf. Chaps. 6, 8, 13) in which $\langle\Omega\rangle^{C}$ is the KE dissipation associated with the mean velocity field (D_{KE}, Fig. 1.1).

The generic MaxEP principle (Chap. 3) also leads to Ziegler's orthogonality condition (non-linear constitutive relations, cf. Chap. 4) for systems arbitrarily far from equilibrium (road *7*). This reduces to linear flux-force relationships (road *8*) in the near-equilibrium limit, $\langle\Omega\rangle \approx 0$, a result that can also be obtained directly from MaxEnt (road *9*, [38–40]). As shown by Ziman [21], Kohler's MaxEP follows rigorously as the mathematical solution to the linearized Boltzmann equation for gas transport; and when expressed in the language of thermodynamic fluxes and forces, it is equivalent to Onsager's MaxEP (road *10*).

In a separate thread, Malkus's dynamical stability analysis [28], involving the same constraints as road *6*, also leads to maximum KE dissipation by the mean flow (road *11*). This raises the possibility of interpreting $\langle\Omega\rangle^{C}$ as a fundamental statistical measure of dynamical stability (road *12*). Intuitively, this might reflect the fact that maximizing $\langle\Omega\rangle^{C}$ ensures that p_{Γ} and $p_{\Gamma*}$ are maximally different, so that entropy-decreasing trajectories that would destabilise the stationary state of maximum entropy production are also maximally improbable. Dynamical stability might also be understood statistically through the 'maximum caliber' interpretation of MaxEnt [39, 44], in which the predicted macroscopic path of a non-equilibrium system is representative of the largest number of plausible microscopic paths. This echoes the interpretation by Malkus [25] that the statistical stability of maximum-dissipation turbulent states reflects the high local density of flow solutions in phase space.

Another direction for future study is the link, if any, between Kohler's MaxEP and radiative MinEP (road *13*). With appropriate constraints, both principles offer solutions to transport problems that can be expressed mathematically as a linearized Boltzmann equation (for mass and radiation, respectively). As far as we are aware, however, a mathematical derivation of radiative MinEP that follows the same lines as the mathematical derivation of Kohler's MaxEP [e.g. 13, 20] has yet to be given explicitly (cf. Chap. 12).

Finally, can MaxEnt provide a theoretical basis for a non-stationary version of MaxEP? (road *14*). A time-dependent formulation of MaxEP is explored by Vallino et al. (Chap. 18) in the context of biogeochemistry; see also [39, 50]. If such a principle could be established, entropy production might be to macroscopic dynamics what the Lagrangian functional is to microscopic dynamics (cf. Chap. 5, Sect. 5.5).

1.5.2 Other Perspectives and Open Questions

So far we have highlighted the role of MaxEnt as a common theoretical framework for some of the principles in Table 1.1. Its potential in this regard stems largely from its generic nature—in all problems the same principle is applied (maximum relative entropy); only the nature of the outcomes i and constraints C differs between problems. Fig. 1.1 offers a tentative road map centred on MaxEnt subject to the specific constraints applied by Dewar and Maritan in Chap. 3 (stationarity, dynamic instability of the MinEP state). In Chap. 7, Niven and Noack apply MaxEnt to flow systems subject to constraints on mean flow rates. There, the interplay between changes in entropy within and outside the system can be described in terms of changes in a potential function, $\Phi = -\ln Z$, where Z is the partition function. By analogy with equilibrium thermodynamics, a principle of minimum[16] Φ for open, stationary systems is proposed, with Φ the non-equilibrium analogue of the Planck potential (or free energy); from this, principles of MaxEP or MinEP might then arise depending on the particular constraints on the system under study. Seleznev and Martyushev (Chap. 5) proposes that MaxEP is an independent physical principle whose theoretical foundation does not rely on MaxEnt at all.

Yoshida and Kawazura (Chap. 15) examine the link between entropy production and stability in a turbulent fluid-plasma system. Using a simple low-dimensional dynamical model, they find that whether the thermal entropy production of the (stable) non-linear stationary state is larger or smaller than the (unstable) linear stationary state depends on the system connectivity (series vs. parallel) and the type of forcing (flux-driven vs. force-driven). Analyses of pipe flow systems show a similar dependence of the relative size of the entropy production rates of laminar versus turbulent flow on the type of forcing [51–54]. Do these results challenge emerging theories suggesting that the most stable states always have the largest entropy production (Chaps. 3, 6, 8 and [28])? Or do the latter theories only apply to selection of one among several non-linear stationary states, and not to selection between one linear state and one non-linear state (Chap. 15)? Alternatively, do these results provide evidence for a principle of minimum Φ, analogous to the minimum free energy principle of equilibrium thermodynamics, that might reduce to MaxEP or MinEP under different circumstances (Chap. 7)?

Boshi et al. (Chap. 10) analyse a GCM incorporating the ice-albedo feedback to show that dynamical transitions between the *snowball* and *warm* stationary climate states are characterised thermodynamically by signature variations in the effective Carnot efficiency of the climate considered as a heat engine. Herbert et al. [49] used a simpler energy balance model to demonstrate a close analogy between the relative stability of snowball and warm states and their thermal entropy production rates, suggesting MaxEP as the relevant selection criterion. A MaxEP principle also appears to govern selection between crystal growth morphologies

[16] The minimum is along a path in the space of flux states.

(Martyushev, Chap. 20). How do these results relate to the theoretical landscape of Fig. 1.1, or to the MaxEP/MinEP dichotomy described above?

The emergence of maximum heat transport as characteristic of stable states in a lattice-Boltmann simulation of Rayleigh-Bénard convection (Weaver et al., Chap. 14) echoes the earlier maximum transport principles of UBT [23]. A subsequent stability analysis by Malkus [25] suggested that, for very high Rayleigh number flows, maximum momentum transport takes precedence over maximum heat transport. How are these results to be reconciled? Does maximum heat transport take precedence at lower Rayleigh numbers?

Clearly, there is much climbing to be done before we reach a consensus view on the theoretical basis of the various MaxEP/MinEP principles described in this chapter. Conquering that lofty peak will require a close interplay between bottom-up and top-down modelling approaches—numerical simulations (GCMs, lattice-Boltzmann models, molecular dynamics simulations), dynamical stability analyses, and variational methods. However, model analyses are not sufficient. Ultimately the models must be confronted with observational data, as exemplified by several contributions to this volume (e.g. Chaps. 11–13, 16, 18, 19). Together, these approaches will continue to provide a fertile testing-ground for emerging theories of MaxEP and other non-equilibrium principles beyond the Second Law.

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