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978-1-107-01968-3 — The Road to Maxwell's Demon
Conceptual Foundations of Statistical Mechanics
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Introduction

> [Classical thermodynamics] is the only theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown.[1]

In these words Albert Einstein expresses an unsolved tension in modern physics, which is the main topic of this book. A central aspect of our experience is that of an arrow of time. We feel a directedness from past to future and we encounter an asymmetry in time of many processes: it is easy to mix coffee with milk, but difficult to un-mix them; it is easy to break a glass or an egg, but hard to bring the pieces back together; people grow older, wood burns, petroleum becomes plastic – with no return. One might expect that these phenomena described by the laws of thermodynamics could be derived from the theories that govern the behavior of the particles that make up all matter. But, surprisingly, this is not the case. These time-asymmetric phenomena seem to have no root in the fundamental theories of physics. In particular, to any thermodynamic evolution that is possible according to the laws of classical mechanics, there corresponds a reversed anti-thermodynamic evolution that is equally possible. For this reason, classical mechanics cannot explain our experience of the thermodynamic asymmetry in time. It is widely believed that the gap between thermodynamics and mechanics can be closed by adding some probabilistic assumptions to mechanics, thus creating the theory of statistical mechanics. But this belief is based on several non-trivial assumptions that have not yet been proved, and there are good reasons to think that they will never be proved.

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[1] Einstein (1970, p. 33)

This book provides a conceptual foundation for statistical mechanics. It shows how the gap between thermodynamics and mechanics comes about, and what is involved in the attempts to close it. The book ends with the conclusion that – contrary to Einstein's claim – thermodynamics is not a "theory of universal content" since it holds only for some special, albeit interesting, cases; and in other cases – especially those known as Maxwellian Demons – it can certainly "be overthrown." It turns out that the attempts to underwrite thermodynamics by statistical mechanics bring out issues that have implications for a variety of questions in physics and in philosophy. In this introduction we first present the problem of the gap between thermodynamics and mechanics, and then describe the general outline of the book.

Towards the end of the nineteenth century, two central theories in physics were put forward: thermodynamics and statistical mechanics. These two theories attempt to explain the same domain of phenomena but some of their predictions turn out to be incompatible with each other. According to the laws of thermodynamics, energy changes its form in such a way that it becomes less useful with time: a magnitude called entropy – which quantifies the amount of energy of an isolated system that cannot be exploited without investing work – increases in the course of time. The laws of thermodynamics were at first considered to be universally and invariably true of our world, without exception. However, it soon became clear that when the atomic structure of matter and the laws of mechanics that govern the motion of particles are taken into account, the thermodynamic laws must be understood *probabilistically*: Boltzmann, Gibbs[2] and other founders of statistical mechanics all agreed that these laws mean that the probability for entropy-decrease is extremely small, but not zero. It is this sort of probabilistic law that Einstein seems to think "will never be overthrown." Indeed, this has been the standard view, more or less, until today. According to that view, it is a consequence of the fundamental laws of statistical mechanics that the probabilistic version of thermodynamics is universally valid; and therefore anti-thermodynamic evolutions in which the entropy systematically and repeatedly decreases without investment of work are impossible.

In 1867, however, James Clerk Maxwell proposed a thought experiment that came to be known as Maxwell's Demon; he proposed this as a counter-example to the laws of thermodynamics in their absolute

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[2] It is not clear whether Gibbs's approach to statistical mechanics is indeed genuinely probabilistic; see Chapter 11.

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(non-probabilistic) version.[3] In Maxwell's thought experiment, "a finite being who knows the paths and velocities of all the molecules by simple inspection"[4] (which William Thomson (Lord Kelvin) called a Demon, although Maxwell insisted that it was a mechanical system[5]) takes a gas in a box at uniform temperature, with a partition in its middle, and manipulates the particles of the gas in such a way that a temperature difference is created between the two sides of the partition. The Demon observes the molecules of the gas, and then opens and closes the partition so that only the fast molecules pass to one side and only the slow ones to the other. After a while the fast molecules are separated from the slow ones, and this means that the temperature of the gas at one side is higher than at the other. The total energy of the gas is conserved, but its distribution changes, in such a way that it becomes more exploitable for the production of work – in clear violation of the laws of thermodynamics. Maxwell's thought experiment is based on the idea that mechanics is universal: there is no "framework of applicability" (to use Einstein's expression) in which the laws of thermodynamics reign and which is not subject to the laws of mechanics. The argument given by Maxwell's Demon implies that a serious adherence to the laws of mechanics entails that the laws of thermodynamics are not universally true.

Maxwell, however, also thought that the predictions of thermodynamics were good enough for many practical purposes: he thought that his Demon could not be practically constructed, for the sole reason that "we are not clever enough."[6] If we were clever enough, nothing in the fundamental laws of physics would stop us from imitating the Demon and acting in an anti-thermodynamic way. For this reason we take Maxwell to challenge also the standard view about the universal validity of the *probabilistic* version of the laws of thermodynamics.

For many years there have been numerous attempts at disproving Maxwell's view.[7] But in 2000 David Albert, in his book *Time and Chance*,[8] proved that Maxwell was right and that a Demon is consistent with classical mechanics. In this book we develop a conceptual framework for statistical mechanics that completes the project initiated by Maxwell

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[3] See Chapter 13 for a detailed presentation of Maxwell's idea.

[4] See Knott (1911, pp. 213–214).

[5] See Knott (1911, pp. 214–215).

[6] See Knott (1911, pp. 213–214).

[7] See Leff and Rex (2003) for an extensive overview and annotated references.

[8] See Ch. 5 of Albert (2000). Albert assumes a view in philosophy of mind that is sometimes called a *physicalist* view (which we accept here) according to which there are no fundamental things or properties in the world that cannot be described by physics (see Chapter 5).

and Albert. Contrary to accepted wisdom, it turns out that a Maxwellian Demon is consistent with the principles of mechanics.

The route to understanding Maxwell's Demon will take us through a number of interesting ideas and open questions in modern physics. For example, we will need to examine the point at which the direction of time enters classical mechanics; the physical origin of macrostates; the meaning of probability in deterministic theories, how it arises, and in what sense it is objective and physical; how to give a physical account of observation, measurement, and memory in classical statistical mechanics; and finally what exactly is a Maxwellian Demon, and why it is consistent with classical statistical mechanics. And there are many other much more detailed questions we shall have to deal with on our way, even only partly, and even though we shall not have answers to all of them.

This book is not meant to replace standard textbooks in statistical mechanics. We focus on the conceptual foundations of classical statistical mechanics rather than on the physical application of the theory. In particular we focus on the question of what it means and what it would take to underwrite thermodynamics by statistical mechanics. These questions are addressed by standard physics textbooks, but some of the basic issues in these discussions are often unclear. For example, it is not always clear what macrostates are and how they come about; nor is it clear what exactly the meaning of probability is in statistical mechanics and how it arises given the deterministic nature of classical mechanics. These are the kinds of questions on which we focus, and we hope that the conceptual clarifications that we offer can then accompany the study of the further details found in standard physics textbooks on thermodynamics and statistical mechanics.

In our discussion we take the fundamental physical theory of the world to be classical mechanics. Of course, in contemporary physics classical mechanics has been replaced by quantum mechanics and the theory of relativity. Nevertheless, focusing on classical mechanics turns out to be fruitful, since the essential problems that arise in underwriting thermodynamics by the current quantum mechanical theory have already arisen in the context of classical mechanics and in almost the same way. And since quantum mechanics itself suffers from some serious interpretational issues, focusing on classical mechanics avoids unnecessary conceptual complexities. We consider some issues related to quantum mechanics in Appendix B.

Let us return to the above-mentioned problem in the attempts to underwrite thermodynamics by statistical mechanics, namely, the

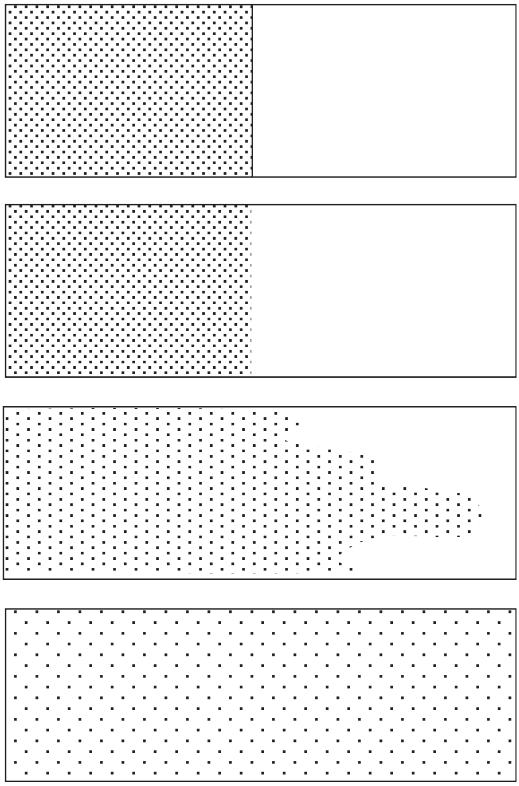

Figure 1.1 Gas expanding in a container

problem of the symmetry of evolutions in time.[9] Consider a film showing a gas expanding in a container; this is illustrated in Figure 1.1. We are all familiar with the plot of the film: in the beginning the gas is confined by a partition to the left-hand side of a container, and when the partition is removed the gas spreads out until, by the end of the film, it fills the entire volume of the container. We can easily tell, simply by looking at the film, whether it is shown in the order in which it was taken, or in the reversed order, i.e. from the end to the beginning. And the reason is that while we often experience processes similar to a gas that spreads out in a box, we never see anything like a gas that evolves spontaneously to a more concentrated state without some external intervention that exerts

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[9] This is perhaps a misnomer: the problem is not about the direction of time itself, but rather about the direction of thermodynamic processes (and in particular of the direction in which entropy increases) in time.

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considerable effort in order to compress it. The evolution in this film is characteristic of thermodynamic evolutions, and the asymmetry that is easily noticed in it is described by the time-asymmetric laws of thermodynamics.

Consider now an altogether different film, one which shows scenes taken from a billiard game. In these scenes we do not see the cues hitting the balls, nor do we see the balls falling into the pockets. We are shown only the parts of the game in which the balls bounce around, colliding with each other and with the rails around the table. Unlike the previous film, in this case we cannot tell whether the film is shown in the forward direction or in reverse. In this sense the billiard balls in this film exhibit a symmetrical evolution with respect to the direction of time. It is this time-symmetric behavior that is stated by the laws of classical mechanics.

The problem of the direction of time in statistical mechanics is the problem of how to reconcile these two apparently inconsistent pictures of the world. The problem is that the time-symmetric behavior of the billiard balls is taken to be characteristic also of the behavior of elementary particles, of which everything is made, including the gas in the first film, where time asymmetry prevails. Since the gas is made of particles, which behave in a time-symmetric way, we would have expected the gas as a whole to behave in a time-symmetric way. The fact that it does not calls for an explanation: how can the underlying symmetric mechanics give rise to the asymmetric phenomena in our experience? What assumptions beyond the time-symmetric laws need be added to mechanics in order to derive the observed thermodynamic phenomena, and on what grounds can these assumptions be justified?

Maxwell's Demon provides a way to understand these questions, since it can reverse the direction of thermodynamic processes: that is, it can effortlessly bring about a compression of the gas, thus reversing the direction in time in which the gas expands, simply by taking seriously the fact that the gas consists of particles that behave like billiard balls. In this book we describe the conceptual foundations of statistical mechanics, including everything that is needed from a physicalist point of view in order to understand the way in which Maxwell's Demon operates. In this sense, the book is a philosophical journey towards Maxwell's Demon. Here is a general outline of it.

In Chapter 2 we present quite briefly some of the main ideas in the theory of thermodynamics that are to be recovered by statistical mechanics. We present three main laws of thermodynamics: the Law of Conservation of Energy, and the two time-directed laws, the Law of Approach to

Equilibrium and the Second Law of Thermodynamics, which describe the thermodynamic asymmetric behavior in time. One main idea we attempt to convey in this chapter is that all the laws of thermodynamics are contingent empirical generalizations, and there is nothing *a priori* or conceptually necessary about them. For although this fact is never explicitly disputed, some arguments in the foundations of statistical mechanics – such as Einstein's words at the opening of this chapter – give the wrong impression that the status of the laws of thermodynamics is much stronger. It is this wrong impression that sometimes makes it hard to accept that Maxwellian Demons are possible. Another major idea we put forward in this chapter concerns the notion of thermodynamic entropy. We show that the physical content of the concept of entropy as characterizing the quality of different forms of energy – that is, as quantifying the degree to which energy can be exploited to produce work – holds only if the time-directed laws of thermodynamics are universally and unequivocally true (in their probabilistic version at least). In cases where the thermodynamic regularities do not hold, such as Maxwell's Demon, entropy no longer has this meaning.

In Chapter 3 we introduce the fundamental ideas of classical mechanics, and show that it is impossible to derive the time-directed laws of thermodynamics, in all their generality, from the laws of mechanics. We begin by introducing the central conceptual tools that will be used throughout the book, namely, microstates (which are the instantaneous states of the universe), the state space (which is the space of all the microstates a system can be in), the accessible region (which is the set of microstates that are compatible with the constraints on the system), macrostates (which are sets of microstates that are indistinguishable by observers, and can sometimes satisfy observable regularities), trajectories (which are the time evolutions of microstates), and dynamical blobs (which are bundles of trajectories all of which originate in some initial macrostate). Using these concepts, we outline the well-known no-go theorem, according to which the principles of mechanics contradict those of thermodynamics, unless the latter are weakened. We describe qualitatively and in outline central theorems in classical mechanics that will be used in later chapters, such as Liouville's theorem, Poincaré's recurrence theorem, and the ergodic theorem.

In Chapter 4 we consider the concepts of time and time-reversal invariance in classical mechanics. We argue that the direction or arrow of time, that is, the very distinction between past and future, is a primitive element of classical kinematics, which is already implicit in the definition of the

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microscopic mechanical state of a particle. Without such an arrow the most elementary mechanical state of a system is not well defined. Once this arrow is given, whether or not thermodynamic systems tend to approach equilibrium in the direction of time that we call from past to future is a matter contingent on the details of the equations of motion and on the initial microstate of the universe (where determinism entails that "initial" here may be any microstate along the trajectory of the universe). The thermodynamic behavior does not determine or define or even characterize the direction of time, which is a fundamental fact described by elementary mechanics. This direction is therefore fixed and given to us before the discussion of underwriting thermodynamics by mechanics even begins.

In Chapter 5 we construct the key notion in statistical mechanics, namely the notion of a macrostate. Macrostates – in our account – are sets of microstates that are indistinguishable by an observer, where this indistinguishability is an objective physical feature of the universe. The thermodynamic macrostates, which are the sets of microstates that appear as having the same thermodynamic properties, have a dual aspect which – we argue in this chapter – accounts for the thermodynamic phenomena. On the one hand, the thermodynamic macrostates are sets of microstates that are indistinguishable from one another by human observers; on the other hand, owing to the dynamics of the universe, these sets of microstates belong to sets of trajectories that satisfy certain dynamical regularities. Although these two features are both present in the thermodynamic macrostates, they are conceptually distinct and independent. Nevertheless, it is their combination that gives rise to the thermodynamic regularities: while the objective dynamical evolution, which determines the regularities, has nothing to do with our observation capabilities, the fact that we, human beings, happen to be able to distinguish between these macrostates explains the fact that we can perceive these regularities. It is the perception of the regularities which underlies the phenomena described by thermodynamics. There may be other sets of microstates that behave in a regular way, but since they do not match our perception, we are not aware of them, and we therefore have no theories about them.[10] We show in this chapter that Boltzmann's famous construction of macrostates, on the basis of his so-called combinatorial approach, is an example of macrostates that have this dual aspect. Since our account of

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[10] Natural selection might explain this fit between the two aspects of the thermodynamic macrostates.

macrostates is based on the notion of indistinguishability, it obviously involves a notion of ignorance: an observer is ignorant about which of the microstates within a given macrostate is the actual microstate of the system. However, this indistinguishability is a consequence of the physical correlations between the observer and the observed system, and therefore we argue that this notion of ignorance is physically objective. Since macrostates are the key notion in statistical mechanics, and since they express the objective correlations between the observer and the observed, our construction of macrostates implies that the observer has an essential status in statistical mechanics. These ideas have implications not only for statistical mechanics but also for the philosophy of mind that we briefly address in this chapter: we show where exactly the mind–body problem enters the discussions of observers and measurement in physics. We believe that this discussion may be fruitful in the context of underwriting the so-called physicalist approach in philosophy of mind, since it addresses the gap between the microscopic physical structure of the world and the way we perceive it.

In Chapter 6 we address the question of how probability as an objective feature of the world arises in classical statistical mechanics on the basis of a completely deterministic dynamical structure. We argue that probability ought to be understood in this theory as transition probability between macrostates. In brief, this idea is as follows: the microstates that start in a given initial macrostate evolve so that their end points, at some given time, form a set that we call a dynamical blob. The probability that a system that starts in a given macrostate will end in some specified macrostate at a later specified time is given by the size of the overlap between that latter macrostate and the dynamical blob. The measure that determines the size of this overlap is chosen so as to fit the observed relative frequencies of macrostates in our past experience of similar evolutions. On the basis of this idea we argue that the size of a macrostate is completely irrelevant to the probability of this macrostate; this conclusion contradicts Boltzmann's view which is empirically inadequate since it inaccurately describes the approach to equilibrium. Our notion of probability suggests that observers who have more detailed observation histories may have an advantage in making accurate predictions, and we illustrate this idea in the case of the spin echo experiments. At the same time, we explain why observation histories do not matter in predicting thermodynamic behavior in normal circumstances. Finally, we address the prevalent understanding of statistical mechanics, based on the idea that the laws of thermodynamics can be underwritten by assuming some special probability distribution over the initial macrostate: although this approach is fundamentally mistaken, we describe in what cases statistical postulates concerning probability distributions over initial conditions can be made meaningful.

In Chapter 7 we apply the conceptual tools developed so far in order to construct the mechanical counterparts of the Law of Approach to Equilibrium and the Second Law of Thermodynamics: these laws are formulated in terms of the transition probabilities between macrostates. Since the notion of entropy is central to these laws, we describe its meaning in statistical mechanics. Thermodynamic entropy quantifies the degree of exploitability of energy, and therefore its proper mechanical counterpart is the degree of control of the system's microstate, and this degree can be expressed in terms of the size of the system's macrostate. The reason is that this size gives the average distance between the macrostate's boundaries, which we can manipulate to some degree, and the actual microstate. The measure which one should use to determine this size ought to be chosen on empirical data based on observations of thermodynamic evolutions. We stress that the measure of entropy is not necessarily the same as the measure of probability: these two measures have different origins, different empirical foundations, and altogether different meanings. Indeed, an important conclusion of our analysis of entropy in this chapter and of probability in the previous chapter is that, in general, entropy and probability are distinct and independent notions, and there is no dynamical or conceptual reason that implies that these two notions relate to each other in some particular way, so that for example macrostates of high entropy are more probable than macrostates of low entropy. On the basis of the notion of entropy, as well as the notion of equilibrium which we also present in this chapter, we outline what needs to be proven in order to establish the statistical mechanical counterparts of the laws of thermodynamics, and we describe an important attempt to do that, namely Lanford's theorem.

In Chapter 8 we distinguish between the formal notion of a probability measure and the notion of physical probability. Since there is an infinite number of probability measures that can be defined over a continuous set of points, such as the state space, we argue that a probability measure may be taken to correspond to physical probability only when the measure turns out to fit the relative frequencies of events in our experience. Therefore the probability measure chosen cannot explain our experience, as argued by the so-called typicality approach in statistical mechanics, but is rather explained by it. In particular, we argue that there are no natural