The Concept of Probability in Statistical Mechanics

D. A. Lavis
Department of Mathematics
King's College, Strand, London WC2R 2LS - U.K.
Email:David.Lavis@kcl.ac.uk

1 Introduction

Thermodynamics was first formulated to describe the thermal properties of matter and, although its scope has now been enlarged, its relationship with the other main theories of physics, general and special relativity, classical and quantum mechanics and elementary particle theory, is still rather uneasy. As Sklar remarks [1, p. 4], it "is surprising that there is any place at all in this picture for a discipline such as thermodynamics" . It could be argued that it was this perception, leading to the conclusion that there is indeed no room for thermodynamics, which was the driving force behind the development of statistical mechanics. Of course, if this point has any weight, it must be seen in the historic context of the late nineteenth century, when attitudes to atomic models were rather ambivalent [1, 2]. Writing in the introduction to his *Lectures on Gas Theory* about the decline of support for atomism in continental Europe, Boltzmann [3, p. 24] remarks (presumably, sadly) that "it has been concluded that the assumption that heat is motion of the smallest particles of matter will eventually be proved false and discarded". The *energeticist* case is presented starkly by Mach:[1]

> The atom must remain a tool for representing phenomena, like functions of mathematics. Gradually, however, as the intellect ... grows in discipline, physical science will give up on its mosaic play in stones.

Maxwell in a letter to Stokes in May 1859 (quoted in [4, p. 91]), about his interest in kinetic theory, emphasizes that he had "taken to the subject for mathematical work" and that he has engaged in his calculations "as an exercise in mechanics". He also remarks that it is perhaps "absurd to ... found arguments upon measurements of strictly 'molecular' quantities before we know whether there be any molecules" (ibid, p. 93). Notwithstanding these reservations he is prepared, in a paper a few years later to mount a spirited defense of atomism [6, pp. 23–87].[2] It is significance that Cercignani [7] has chosen to subtitle his biography of Boltzmann *The Man Who Trusted Atoms*. In his paper of 1872, deriving the transport equation and H-theorem, Boltzmann [6, pp. 188–193] certainly writes as if he 'believes in' the molecules of the mechanical theory of heat. However, in his *Lectures on Gas Theory*

[1] Taken from Mach's *Popular Scientific Lectures* (1894) and quoted in [2, p. 21] .

[2] Papers by Maxwell, Clausius, Poincaré, Zermelo and Boltzmann are contained (in English translation where necessary) in the two volumes by Brush [5, 6] and will be cited accordingly.

[3][3] he takes a slightly more cautious stance. The title of the first section of the introduction is 'Mechanical analogy for the behaviour of a gas' and in that section [3, p. 21] he remarks that: "Energetics is certainly very important for science; however, up to now its concepts are still rather unclear, and its theorems not very precisely expressed, so that it cannot replace the older theory of heat".

Aside from the question of atomism versus energeticism the very existence of *statistical* mechanics could be viewed as a failure of some putative programme for the replacement of thermodynamics by a form of many-body mechanics, be it classical or quantum. An extra ingredient has been used to bridge the gap from purely mechanical concepts, like position and momentum, to the thermodynamic quantities of pressure, temperature and entropy.

2 From Kinetic Theory to Statistical Mechanics

The power of an atomistic approach was evident as early as 1738 when Bernoulli, in his *Hydrodynamics*, was able to derive Boyle's law by assuming a gas of particles all with identical velocities. He was also able to obtain the formula relating temperature to particle velocity. By the time of Clausius and Maxwell it was recognized that there would be variations in the velocities of gas particles. While Clausius [5, pp. 111–134] replaced the velocities by their average value, Maxwell [5, pp. 148–171] proposed a formula for velocity variation. Writing to Stokes in 1859 he remarks that of course his particles "have not all the same velocity, but the velocities are distributed according to the same formula as the errors are distributed in the theory of least squares".[4] The resulting formula was the, now famous, *Maxwell law* that, for a gas of N small, hard, perfectly elastic spheres acting on one another only during impact, the number of spheres whose speed[5] lies between v and $v + \mathrm{d}v$ is $f_1^{(\mathrm{M})}(v)\mathrm{d}v$, where

$$f_1^{(\mathrm{M})}(v) = \frac{4N}{\alpha^2\sqrt{\pi}}\, v^2 \exp\left(-\frac{v^2}{\alpha^2}\right).$$

It is of some interest that the word 'probability' does not occur in this part of the paper, making its appearance only at the point where Maxwell considers particle collisions. However, it would be difficult to draw a conclusion from this observation and it can be fairly said [1, p. 30] that we find in Maxwell's paper "language of sort that can be interpreted in a probabilistic or statistical vein".

When considering the origin of the insertion of probabilistic ideas into many-particle dynamics, we must examine, not only equilibrium distributions, but also the theory of transport processes, the foundations for which were laid by Maxwell [6, pp. 23–87] and developed by Boltzmann.[6] Boltzmann's analysis starts with the distribution function $f_1(\mathbf{v}, t)$ so that $f_1(\mathbf{v}, t)\mathrm{d}^3v$ is the number of particles in the volume element d^3v at the point $\mathbf{v}$ in the single-particle velocity space at

[3] Published in the same year as Zermelo's criticism [6, pp. 208–217] of his H-theorem results.

[4] Taken from *The Scientific Letters and Papers of James Clerk Maxwell* edited by P. M. Harman and quoted in [4, p. 95] .

[5] Maxwell calls v the "actual velocity" of the sphere, but in the context of his derivation it is clear that the quantity is what we would now call the speed, since he remarks that the "velocities range from 0 to ∞".

[6] Boltzmann papers on this subject began in 1868, but the most compact presentation of his work is given in his *Lectures on Gas Theory* [3].

time t.[7] To calculate how this distribution changes with time we need an expression for the number of pairs of particles with two different velocities which collide in unit time.[8] Such information will be contained in the two-particle velocity distribution function $f_2(\mathbf{v}, \mathbf{v}', t)$. The fundamental assumption that Boltzmann makes here is that there are no correlations between velocities. This means that $f_2(\mathbf{v}, \mathbf{v}', t) = f_1(\mathbf{v}, t) f_1(\mathbf{v}', t)$. This *molecular chaos condition* is assumed to persist for all time and enabled Boltzmann [6, pp. 188–193] to derive his transport equation, which has a solution which is independent both of time and the velocity direction and corresponds to the Maxwell distribution. However, Boltzmann aimed to prove something stronger, namely to show that the Maxwell distribution is the *unique* stationary solution that will be monotonically approached from any non-equilibrium distribution. He was able to do this [6, pp. 188–193] by proving the H-theorem, which established that the quantity

$$H(t) = \int \mathrm{d}^3 v f_1(\mathbf{v}, t) \ln[f_1(\mathbf{v}, t)],$$

decreases monotonically with time, with the only solution of $\mathrm{d}H/\mathrm{d}t = 0$, being the Maxwell distribution.

It is fairly clear that, up to this point, the subject under discussion is still 'kinetic theory'. Although the language and concepts of Maxwell and Boltzmann have a certain probabilistic flavour the distribution functions are still meant to be a measure of the actual number of particles with velocities in a particular range. The turning point and the perceptual change seems to have been driven by the criticisms of Boltzmann's results.

As indicated above, the scientific orthodoxy in Germany in the late nineteenth century was energetics, and this provided a constant challenge to the nascent kinetic theory. This challenge was compounded by two technical objections.

The first of these concerns the problem of reconciling the reversibility of mechanical laws and the irreversibility of natural processes as described by the second law of thermodynamics. This seems to have been first noted by Maxwell [4, p. 141], but it came to Boltzmann's attention in two papers published by Loschmidt [8].

In response to some work of Poisson, Poincaré [6, pp. 194–202] proved the *recurrence theorem* that now bears his name[9] and in a second brief paper he drew attention to what became the second problem in reconciling thermodynamics and kinetic theory [6, pp. 203–207], namely the incompatibility of the second law of thermodynamics and the mechanical theory of heat which is based on a usually recurrent dynamic system. This second paper seems to have been ignored both by Boltzmann and by Zermelo [6, pp. 208–217] who, in making a similar point elicits a reply from Boltzmann [6, pp. 218–228], followed by further dialogue ([6, pp. 229–237] and [6, pp. 238–245]).

[7] In his first presentation of the calculation in 1872 [6, pp. 188–193] the distribution was taken to be over energies, but this was modified by the time of the 1896 lectures.

[8] In his original derivation of his transport equation Boltzmann neglected the existence of particle collisions involving more than two particles.

[9] For a mechanical system there are an infinite number of ways of choosing initial conditions such that the system will return infinitely many times as close as we like to the initial position. There are also an infinite number of initial choices which do not have this property, but the latter are 'exceptional' in comparison with the former.

Boltzmann makes a number of points related both to the recurrence problem and to the question of irreversibility:

(i) If the number of molecules is infinite then the Poincaré theorem does not apply and, even for a 'small' system,[10] the recurrence time would be a number in seconds with "many trillions of digits".

(ii) In practice we would not expect a finite system to be completely isolated so again the Poincaré theorem does not apply.

(iii) The second law is, from the molecular viewpoint, a statistical law.

(iv) In order to understand irreversibility it is necessary to be able to distinguish clearly between the macroscopic and microscopic levels and to have a definition, for the dynamic system, of what is meant by a macrostate.

The importance of these replies can be seen in the fact that they have each, in different ways, led to the development of programmes for non-equilibrium statistical mechanics. With the possible exception of (iii), they are also still subjects of dispute.

The question of whether statistical mechanics applies only to systems of a large, possibly infinite, number of microsystems will be discussed below. The view that external influences are needed to achieve statistical mechanical equilibrium[11] takes two forms. The disturbance could be of the form of small random perturbations which, as envisaged by Boltzmann, will alter the trajectory of the system and prevent recurrence and reversibility. Or it could be a steady dissipation of energy. The remark by Sklar [1, p. 156] that "within the context of the dynamical theory of non-equilibrium ... the equilibrium state exists as the 'attractor' to which the dynamics of non-equilibrium drives [it]", would imply something of this sort, since isolated mechanical systems do not have attractors [9].

In his reply to Loschmidt, Boltzmann [6, pp. 188–193] argues for a statistical view of the second law. Writing in the following year a similar point is made by Maxwell. In his review of Tait's *Thermodynamics* he notes that the "truth of the second law", as a statistical theorem, was "of the nature of a strong probability ... not an absolute certainty" like dynamic laws, (quoted in [4, p. 141]). The most immediate effect of this can be seen in a change of perception of the meaning of $f_1(\mathbf{v},t)$. This function is no longer regarded as the actual distribution of the N particles of the gas. In modern terms it has become equal to $N\rho_1(\mathbf{v},t)$, where $\rho_1(\mathbf{v},t)$ is the single-particle probability density function over velocity space. From this point it is a relatively small step to change the quantity of interest to $\rho_N(\mathbf{x},\mathbf{p},t)$, the probability density function on the phase space Γ of the vector $(\mathbf{x},\mathbf{p})$, specifying the coordinates and momenta of all the degrees of freedom of the N particles. If the system is Hamiltonian and if probabilities are preserved by the Hamiltonian flow then the probability density function must satisfy Liouville's equation. This equation provides the starting point for a number of different approaches to non-equilibrium statistical mechanics, most notably the derivation of the Bogolyubov-Born-Green-Kirkwood-Yvon hierarchy of kinetic equations and the work of the Brussels-Austin School, which will be discussed in Sec. 6. However, for the moment we are interested in possible interpretations of the probability density function $\rho_N(\mathbf{x},\mathbf{p},t)$ and we must first consider the options available to us.

[10] Which he takes to be 1 c.c. of air containing 10^{18} molecules [6, pp. 218–228].

[11] Called by Sklar [1, p. 250] the *interventionist approach*.

3 Different Views of Probability

There seem to be three attitudes to the presence of statistics in statistical mechanics. The first, which tends to be that adopted by classical texts in the subject and to go with great reliance on the concept of *ensembles*, is to regard the subject algorithmically, as a procedure for arriving at answers, rather in the same way as the *replica method* is used in some calculations in critical phenomena and neural networks. Thus Tolman [10, pp. 1,2] writes:

> [The] principles of statistical mechanics are to be regarded as permitting us to make reasonable predictions as to the future of a system. ... [They consist] in abandoning the attempt to follow the precise changes in state which take place in a particular system, and in studying the behaviour of a collection or *ensemble of systems*.[12]

The second approach, is to regard probabilistic ideas rather in the way that the energeticists regarded the atom (see the quote from Mach given above), as something that a more mature science would be able to discard. The means for doing this is usually thought to be *ergodic theory*, which will be considered in detail below.

The third approach is to take a more positive attitude to the probabilistic ideas, interpreting them, by implication if not explicitly, according to one of the standard view of probability. In this context, therefore, we shall now review the different views of probability. There are many ways to subdivide these views [1, 12, 13]. The main division is between the *scientific (or objective) view* and the *subjective view*. We shall make a further subdivision of each of these categories.

3.1 The Scientific View

This may be characterized by the fact that it considers "the theory of probability as a science of the same order as geometry or theoretical mechanics", [14, p. vii]. Thus probability is an objective property. But of what? Clearly not simply of an object, like a die, without any other qualification. It seems most reasonable to define the probability as that of the outcome of a particular *experiment* with the object in question, in circumstances where some aspect of the test is *incompletely specified*. Typically this incomplete specification arises because the outcome is sensitive to initial conditions, so that it is, both in practice and in principle, impossible to fix all the aspects of the experiment necessary to determine the outcome. In the case of the throw of a die,[13] we are unable to determine which side finally lands uppermost, because we are unable to to specify exactly the initial location and orientation, and angular and linear acceleration.[14] As we have seen in relation to the comments on Tolman, given above, there is a tendency to talk of 'incomplete knowledge' rather

[12] In the same passages he also refers to 'incomplete' and 'partial' knowledge. The has led Hobson [11], an adherent of a subjectivist view of probability in statistical mechanics, to claim him as a supporter. We do not find this claim entirely convincing [12]. The passage could quite easily be read as a statement of the (presumably) uncontentious view that probability concepts are used when a system is incompletely specified.

[13] And excluding the possibility of careful dropping it with one face uppermost onto a yielding surface.

[14] Neither are we able to control the outside effects such as air resistance and wind. However, this is a separate issue leading us to the question of the role of the isolation or non-isolation of the system.

than 'incomplete specification'. However, for an objectivist such terminology would be regarded as misleading.

We now have the problem of *defining* probability and there are two ways in which this is done in the objective context.

The Relative Frequency Interpretation. In this tradition the probabilistic properties of a system are *defined* by considering the results of a large number of macroscopically identical experiments on the system. For von Mises [14, p. 29] this large number of operations or events is the *collective*; the probability of a particular outcome is then defined as the limit of the *relative frequency* of this outcome in the collective, as the size of the collective increases to infinity. Probability then is, in some sense, not a property of a single experiment, but of the collective of experiments.

The Propensity Interpretation. For Popper [15, 16] (see also [13]) probability is a *latent propensity* of an individual system experimented on in a specified way. In keeping with his general views on the philosophy of science, the probability of the outcome of an experiment is something about which one forms a hypothesis, which is then tested by repeated experiments.

3.2 The Subjective View

According to this view the probability that someone assigns to an event is a measure of her/his degree of belief in the outcome. For some people the adoption of the viewpoint is a liberating experience. As E. T. Jaynes writes [17, p. 268]:

> As soon as we recognize that probabilities do not describe reality – only our information about reality – the gates are wide open to the optimal solution of problems of reasoning from that information.

Again we shall make two subdivisions of this viewpoint.

Degrees of Belief Interpretation. This view, which is usually associated with names of Ramsey and de Finetti, allows one to hold any coherent set of beliefs about the probabilities of the outcomes of events. Coherence is described using the *Dutch book arguments* which concern willingness to bet. The constraints provided by these arguments prevents one holding beliefs which would mean that one inevitably looses money and leads to probabilities which satisfy the usual rules of the probability calculus. I agree with Hobson [11, p. 33] that this type of subjectivism has no relevance for the physical sciences and it will not feature any further in our discussion.

Rational Belief Interpretation. This point of view, which is sometimes called 'objective Baysianism' has already been introduced by a quote from Jaynes. Probability is still a question of belief, but it is constrained to be rational belief, not only in the Dutch book sense, but by having taken into account in a systematic way, all the evidence available. The principle exponent of this point of view is E.

T. Jaynes.[15] His method, now usually called the *maximum entropy method*, will be discussed in relation to statistical mechanics below. It has, however, been applied by him in other situations as well. In it simplest form, when no information on which to base our probabilities is available, the rational choice is in accord with the Keynesian *principle of indifference* [19]. However, the application of this principle is not straightforward. Although it leads to the choice of a uniform distribution, the variable with respect to which the distribution is uniform is not always obvious. Jaynes resolution of this problem is to argue that, if probability is to be assigned according to our state of knowledge of the system, then *it must be assigned in the same way to equivalent problems.* The probability assignment must be invariant under all transformations between equivalent problems. He illustrates his method by proposing a solution to the Bertrand chord problem, [18, p. 131], showing that his solution is supported by a relative frequency test?

4 Ergodic Theory

Consider again a Hamiltonian system with configuration vector $\mathbf{x}$ and momentum vector $\mathbf{p}$. Then the time evolution of the system is given by vector $(\mathbf{x}(t), \mathbf{p}(t))$ in Γ, moving according to the Hamiltonian flow. Given a measure density function $\mu(\mathbf{x}, \mathbf{p}, t)$, the Hamiltonian flow is measure-preserving if $\mu(\mathbf{x}, \mathbf{p}, t)$ satisfies Liouville's equation. This will be the case for the uniform volume measure. So if γ is a subset of Γ, which is invariant under the Hamiltonian flow and of finite volume $M(\gamma)$ we can define the time-independent normalized measure function $\mu(\mathbf{x}, \mathbf{p}) = 1/M(\gamma)$, for $(\mathbf{x}, \mathbf{p}) \in \gamma$, and zero for $(\mathbf{x}, \mathbf{p}) \notin \gamma$. This mechanical system is related to a thermodynamic system through correspondences between thermodynamic quantities $\{Q_{\mathrm{T}}\}$ and mechanical phase functions $\{Q(\mathbf{x}, \mathbf{p})\}$.

The starting point for ergodic theory is to argue that Q_{T} is equal to the average $\widetilde{Q}(\mathbf{x}_0, \mathbf{p}_0, \tau)$ of Q over a period of time τ, computed along the path of the system from $(\mathbf{x}_0, \mathbf{p}_0)$. It is assumed that τ is long with respect to the microscopic correlation time, the relaxation time of macroscopic variables and the time taken to destroy purely local constants of motion. From this it is argued that the result of a measurement is effectively the infinite time average obtained in the limit $\tau \to \infty$.[16] For this to be useful it is necessary to establish that this limit exists and that it is independent of $(\mathbf{x}_0, \mathbf{p}_0)$. It was shown by Birkhoff [20] that $\lim_{\tau \to \infty} \widetilde{Q}(\mathbf{x}_0, \mathbf{p}_0, \tau) = \widehat{Q}(\mathbf{x}_0, \mathbf{p}_0)$ exists almost everywhere in γ; that is except possibly for a set of μ-measure zero. From this it follows (see e.g. [12]) that $\widehat{Q}$ is a constant of motion almost everywhere in γ. Now let $\overline{Q}$ be the average of Q over γ with respect to μ. It also follows from Birkhoff's theorem that $\overline{Q} = \overline{\widehat{Q}} = \widehat{\overline{Q}}$ and it is clear that, if $\widehat{Q}$ is a constant almost everywhere in γ, $\overline{\widehat{Q}} = \widehat{Q}$ and $\widehat{Q} = \overline{Q}$ holds almost everywhere in γ. If this is the case then $\widehat{Q}$ is a constant almost everywhere in γ. *If $\widehat{Q} = \overline{Q}$ holds almost everywhere in γ, for all phase functions integrable over γ, then the system is said to be ergodic.* Thus for ergodic system we can (almost) legitimately identify Q_{T} with $\overline{Q}$.

[15] For his collected papers until the date of its publication see [18]. For convenience all references to Jaynes' work will be made to this collection rather than to the original source of the paper.

[16] The obvious problem with this is that, if it were true, we should never be able to make measurements on non-equilibrium systems [1, p. 176].

It would be tempting to suppose that ergodicity has established the connection between thermodynamic quantities, defined as time averages, and phase averages, without the need to interpret the measure density function μ. We do, however, have the problem of the set of μ-measure zero. To know that this set can be neglected we must know that a measurement is never (or hardly ever) made starting at one of its points. This brings us back to assuming some sort of probabalistic interpretation for μ. We have not escaped the statistics in statistical mechanics.

Given that ergodic theory is not an escape from probability, it is still worth considering how, at least for objectivists, it can be used as a justification of the probability measure chosen. The original *ergodic hypothesis*[17] assumed that the path of the system passed through every point of γ. It is clear both that this would be sufficient to establish ergodicity and also that it cannot be true [12]. The alternative *quasi-ergodic hypothesis* that the path passes arbitrarily close to every point of γ has not proved sufficient to establish ergodicity, although it is necessary.

There is, however, a condition, both necessary and sufficient, which is intuitively somewhat similar to the quasi-ergodic hypothesis. To prove the necessity of the latter we would assume that, given a particular path of the system, there exists a point in γ which has a neighbourhood not containing any points of the path. This is clearly impossible for an ergodic system since we could alter the phase average, without changing the time average, by changing the value of the phase function in the neighbourhood. The even stronger assumption that γ can be decomposed into two subsets of non-zero measure, invariant under the flow, is clearly inconsistent with ergodicity. *Metric transitivity*, which is defined as the negation of this assumption, is thus necessary for ergodicity and it is not difficult to see that it is also sufficient.

5 Equilibrium Statistical Mechanics

This works very well; supporting, among other things, the enormous development, since the early 1970's, in the theory of phase transitions. One reason for this success is that, in spite of unresolved problems about the foundations, the superstructure is based on a few agreed propositions. Firstly on the fact that equilibrium corresponds to having a probability density function ρ which is not an explicit function of time and secondly on the form for ρ which should be used in given sets of physical circumstances.

The way that, such sets of circumstances are determined and interpreted by the subjectivists will be discussed below. We should, however, note that if the energy, given by the value of the Hamiltonian, is the only isolating constant of motion,[18] then there is general agreement that the appropriate probability density function is the one obtained by applying equal probabilities to the points of an accessible region of phase space. This leads to the microcanonical distribution and the simplest way to derive it [21] is to take the invariant set γ, defined in Sec. 4, to be the shell $E < H(\mathbf{x},\mathbf{p}) < E + \triangle E$. The distribution over the energy surface Σ_E is then induced in the limit $\triangle E \to 0$. From this the canonical distribution can be derived

[17] Usually attributed to Boltzmann, but see the translator's introduction to [3].

[18] An integral of the equations of motion does not necessarily define a surface in Γ. Only those which do can be used to reduce the dimension of a set invariant under the flow. Such an integral is called an *isolating constant of motion.*

using either the central limit theorem [21] or the method of steepest descents [22]. Both these procedures are asymptotically valid for systems with a large number of microsystems. Subjectivists do not need this limit, although "many quantities of interest are highly predictable when N is large" [11, p. 70].

So, although it is viewed in different ways according to one's view of probability, the starting problem for equilibrium statistical mechanics amounts to having a means of justifying the use of the uniform distribution over an energy shell. We see that ergodic theory will 'almost' give us such a justification if the Hamiltonian is the only isolating constant of motion, since then we might expect the energy surface to be metrically transitive. However, the problem of proving the non-existence of additional isolating constants of motion is, in general, very difficult and when they exist the form of thermodynamics differs significantly from the standard form [23, 24]. To whom is this important? Not, I think, to those like Tolman [10], who regard the object of statistical mechanics not as a single system, but an *ensemble of systems.* Choosing to model the ensemble by the microcanonical distribution is simply to include in the ensemble systems with all values of the other unknown isolating constants of motion.

As we saw above, Boltzmann aimed to justify the Maxell distribution by showing that it arose as the stationary solution to his transport equation which is attained in the limit $t \to \infty$. There are two substantial programmes which follow a similar route in aiming to show that equilibrium arises in the long-time limit from non-equilibrium situations. These are that of the Brussels-Austin School [25, 26], and that using the maximum entropy method [11, 17, 18].[19] The work of the Brussels-Austin School is most appropriately considered in the context of non-equilibrium theory in Sec. 6. However, the maximum entropy method has a form specifically for equilibrium and this we shall now discuss.

Jaynes [18, p. 416] prefers to refer to his method as "predictive statistical mechanics" and he goes on to say that:

> [It] is not a physical theory, but a form of statistical inference....instead of seeking the unattainable [it] asks a more modest question: "Given the partial information that we do in fact have, what are the best predictions we can make of observable phenomena?"

So the fact that there are *unknown* constants of motions is irrelevant, since our only task is to make predictions based on what we know.[20]

We now compare the maximum entropy formulation with a standard, objectivist, formulation for a simple problem. We consider a system with discrete energy levels $\{E_1, E_2, \ldots, E_n\}$. Then questions are posed in the following ways:

(i) *In the maximum entropy formulation:* What is the *best* probability distribution for the random variable E, the energy of the system, based on the information available to us?

(ii) *In an objectivist formulation:* Given the physical environment of the system (whether it is isolated, or in contact, in some way with its exterior), what is *the* probability distribution for E?

[19]These two approaches are discussed and compared by Dougherty [27, 28].

[20]As we see below, he argues in a similar way in relation to unknown degrees of freedom, when he discusses the non-objective nature of entropy.

For Jaynes the key to the problem is the idea of *uncertainty.* Given an appropriate measure of uncertainty, if we choose the probability distribution which maximizes the uncertainty relative to the available information then this will be the *best* probability distribution because it assumes as little as possible. He shows [18, p. 16] that the unique measure of uncertainty, which satisfies some reasonable mathematical properties, is Shannon's *information entropy*

$$S_{\mathrm{I}}(p_i) = -\sum_{i=1}^{n} p_i \ln(p_i)\,,$$

[30]. The information entropy S_{I} is then related to the thermodynamic entropy S_{T} by $S_{\mathrm{T}} = k_{\mathrm{B}}\{S_{\mathrm{I}}\}_{\mathrm{Max}}$. Consider the following two cases:

We know nothing about the state of the system, other than the number of energy levels.

(a) Since the system has no dynamics there is no way of 'deriving' the probability distribution. However, an *objectivist* will believe that there *is* a probability associated with an experiment to determine its state. In both versions of objectivism repeated experiments will be made. In the case of a relative-frequentist this will serve to define the probability; someone who holds a propensity view will have formed a hypothesis, the most reasonable being that $p_i = 1/n$, and the sequence of experiments will be used to see if the hypothesis is falsified.

(b) Using the *maximum entropy method* we maximize $S_{\mathrm{I}}(p_i)$ subject only to the condition $p_1 + p_2 \cdots + p_n = 1$ to give the same result as that hypothesized by the objectivists.

This is the *uniform distribution.*[21]

For the canonical distribution the objective and subjective statements of the problem differ.

(a) The objective statement here has a thermodynamic content. The system is taken to be in a heat-bath at temperature T, which is the conjugate variable to the energy E. Then the most elegant way to derive the required results in this case is, as for the Hamiltonian system described above, to use the central limit theorem [29].

(b) For the maximum entropy method the equivalent situation is to know the expectation value $\langle E\rangle$ of the energy. Then $S_{\mathrm{I}}(p_i)$ is maximized subject to the normalization condition and $p_1E_1 + p_2E_2 + \cdots + p_nE_n = \langle E\rangle$ to give

$$p_i = \frac{\exp(-E_i\lambda)}{Z(\lambda)} \quad \text{where} \quad Z(\lambda) = \sum_{i=1}^{n}\exp(-E_i\lambda), \quad \langle E\rangle = -\frac{\mathrm{d}\ln(Z)}{\mathrm{d}\lambda}.$$

There are a number of problems with Jaynes' method which can be discussed in reference to this example. Two of these are:

[21] It is similar to the microcanonical distribution, which is the uniform distribution over the degenerate states corresponding to an energy level in which the system is known to be.

A conceptual problem concerns the status of entropy. It can be expressed in the following way:

- The object of interest for statistical mechanics is a system $\mathcal{O} = \{\mathcal{O}_{\mathrm{M}}, \mathcal{O}_{\mathrm{T}}\}$, where $\mathcal{O}_{\mathrm{M}}$ denotes the qualities at the micro (atomic) level and $\mathcal{O}_{\mathrm{T}}$ denotes the qualities at the macro (thermodynamic) level.
- About such a system we have a certain amount of information $\mathcal{I} = \{\mathcal{I}_{\mathrm{M}}, \mathcal{I}_{\mathrm{T}}\}$.
- For such a system we devise a model $\mathcal{M} = \{\mathcal{M}_{\mathrm{M}}, \mathcal{M}_{\mathrm{T}}\}$.

What is it that has entropy? There would probably be agreement that the entropy $S(\mathcal{O}_{\mathrm{M}})$ is not well-defined, but does the entropy $S(\mathcal{O})$ exist? Entropy is defined in terms of a probability distribution so if you believe that the distribution is an objective property of the system (including its environment) there is no problem in saying that $S(\mathcal{O})$ exists. Jaynes would deny this. For him the entropy is $S(\mathcal{I})$. He argues that you can never know what degrees of freedom a system has. You may, for example, have neglected internal degrees of freedom within your molecules which would make a contribution to the entropy. So entropy is not an 'objective' property of the system. It is 'subjective' in the sense that it is a function of the knowledge which you, the subject, have. The counter argument would go something like this. Yes, but what you are calculating is $S(\mathcal{M})$ the entropy of your model, which as long as you have carried out an exact calculation *is* the entropy of the model, however good or bad it is, for the system you are considering. The Sackur-Tetrode equation gives the correct entropy of a perfect gas in spite of the fact that perfect gases do not exist. The relation between $S(\mathcal{M})$ and $S(\mathcal{O})$ is the same as between any two other theoretical and physical quantities and doesn't lead to the rejection of the existence of $S(\mathcal{O})$.

A mathematical problem associated with Jaynes' method was first raised by Friedman and Shimony [31]. Consider the system, described above, with energy spectrum $\{E_1, \ldots, E_n\}$ and suppose and that we are first given the background datum $\mathcal{D}_0$, that contains no information apart from its structure (the number of states). Then, as we saw above, from the maximum entropy principle, the appropriate distribution is the uniform distribution $\mathrm{Prob}[E_j|\mathcal{D}_0] = 1/n$. Suppose now the energy E is measured and let the datum be $\langle E \rangle = U$, where U is given. Referring to this new piece of datum as $\mathcal{D}_1$ and using the maximum entropy principle we now have the canonical distribution $\mathrm{Prob}[E_j|\mathcal{D}_0 \,\mathrm{and}\, \mathcal{D}_1] = \exp(-E_j\beta)/Z(\beta)$. Now according to the usual formula for conditional probabilities (Bayes' Theorem)

$$\mathrm{Prob}[E_j|\mathcal{D}_0] = \sum_{\mathcal{D}_1} \mathrm{Prob}[E_j|\mathcal{D}_0 \,\mathrm{and}\, \mathcal{D}_1]\mathrm{Prob}[\mathcal{D}_1|\mathcal{D}_0]$$

and since $\mathcal{D}_1$ varies over all values of β it can be supposed to have a probability density function $p(\beta)$, giving

$$\frac{1}{n} = \int \mathrm{d}\beta p(\beta)\frac{\exp(-E_j\beta)}{Z(\beta)}, \qquad 1 \leq j \leq n.$$

But for $j = 1$ and all $p(\beta)$, except $p(\beta) = \delta^{\mathrm{D}}(\beta)$

$$\int \mathrm{d}\beta p(\beta)\frac{\exp(-E_1\beta)}{Z(\beta)} > \int \mathrm{d}\beta p(\beta)\frac{\exp(-E_1\beta)}{n\exp(-E_1\beta)} = \frac{1}{n}.$$

This problem has generated a lot of discussion (see [32]). The response by Jaynes [18, p. 250] was that "if $\mathcal{D}_1$ is a statement about a probability distribution on the sample space $\Sigma = \{E_1, \ldots, E_n\}$, then it can be used as a constraint when maximizing entropy but not as conditioning statement in Bayes' theorem, since it is not a statement about an event in Σ. On the other hand, if $\mathcal{D}_1$ is a statement defining an event in the sample space Σ^m of m trials, then the converse is the case".

6 Non-Equilibrium Statistical Mechanics

In the final chapter of his seminal work on the philosophical foundations of statistical mechanics Sklar [1] begins a summing up of the current state of the area by stating that, in his opinion, "most important questions still remain unanswered in very fundamental and important ways". Although, as we have seen, this is to some extent true for equilibrium it is more evidently the case for non-equilibrium.

It seems to be the case that the attempt to remove the statistics from statistical mechanics (via ergodic theory and associated dynamic analysis) is now at a dead-end. So when we are considering the way a system behaves over time the "evolution we describe ... will be that of a probability distribution over microstates of systems compatible with the macroconstraints defining the systems of interest" [1, p. 261]. There, therefore, remains the question of the interpretation of probability. Or, at least, whether you want to embrace a subjective view of probability. Because, as we shall see, if you do that you will be able to develop a type of solution to the problem of entropy increase and the evolution to equilibrium which would not make sense to an objectivist. On the other hand most of the approaches to this problem proposed by objectivists could be regarded as 'interpretation-free'.[22]

One group who would probably disagree with Sklar as to the unresolved nature of the problem of irreversiblity are those like Lebowitz [33] and Bricmont [34], who believe that the problem was solved in a satisfactory way by Boltzmann, and that current problems are caused by the fact that he has been misunderstood. The 'successful' explanation is based on the implementation of the procedure[23] for defining macrostates by dividing the phase space into small cells. This *course graining* approach works very well, in the sense that it gives a clear (possible) physical insight into the mechanism at work in irreversiblity. The usual objection is to the rather arbitrary nature of the course graining procedure. This is acknowledged by Lebowitz who says that while "this specification of the macroscopic state clearly contains some arbitrariness, this need not concern us too much, since all the statements we are going to make about the evolution of [the macrostate] are independent of the precise definition as long as there is a large separation between the macro and microscales" [33, pp. 33–34].

Lebowitz's article elicited a number of letters in Physics Today, two of which are of particular interest since they represent the main competing schools in non-equilibrium theory. The first, from Barnum *et al.* [36] criticizes Boltzmann's ideas from the perspective of "Shannon's statistical information and Edwin Jaynes' principle of maximum entropy". The criticism here, as I understand it, is not so much

[22] This is a view I expressed [12] with regard to the work of Progogine. It was subsequently endorsed by Dougherty [27].

[23] More fully developed by Paul and Tatiana Ehrenfest [35].

of course-graining *per se* as of the underlying philosophy. In fact Jaynes is on the whole favourable to Boltzmann's approach, giving an account of it, together with the comment that, in "Boltzmann's method of most probable distribution, we have already the essential mathematical content of the principle of maximum entropy" [18, p. 227]. However, this kind of approach is not the way Jaynes seems to prefer to describe increase of entropy. The following is the account given in [18, p. 27].

6.1 A Subjectivist Approach to Non-Equilibrium

Entropy is a measure of uncertainty or lack of information. As time passes our information about the system becomes out of date. There is a loss of information, which is an increase in uncertainty (entropy). This perception is realized in the following way. Suppose we have a set $\{\Omega_1(t), \ldots, \Omega_m(t)\}$ of time-dependent observables related respectively to the phase functions $\{\omega_1(\mathbf{x}, \mathbf{p}; t), \ldots, \omega_m(\mathbf{x}, \mathbf{p}; t)\}$ by

$$\Omega_j(t) = \langle \omega_j(\mathbf{x}, \mathbf{p}; t) \rangle = \int_\Gamma \rho(\mathbf{x}, \mathbf{p}; t) \omega_j(\mathbf{x}, \mathbf{p}; t) \mathrm{d}\Gamma.$$

Measurements are made of these observables at the time t_0 with the results $\{\overline{\Omega}_1(t_0), \ldots, \overline{\Omega}_m(t_0)\}$. The probability density function $\rho(\mathbf{x}, \mathbf{p}; t_0) = \rho_0(\mathbf{x}, \mathbf{p}; t_0)$ is the one which maximizes

$$S(\rho(t_0)) = -k_\mathrm{B} \int_\Gamma \rho(\mathbf{x}, \mathbf{p}; t_0) \ln\{\rho(\mathbf{x}, \mathbf{p}; t_0)\} \mathrm{d}\Gamma,$$

subject to the constraints

$$\overline{\Omega}_j(t_0) = \int_\Gamma \rho(\mathbf{x}, \mathbf{p}; t_0) \omega_j(\mathbf{x}, \mathbf{p}; t_0) \mathrm{d}\Gamma.$$

The probability density function evolves according to Liouville's equation and at a later time t is given by $\rho_0(\mathbf{x}, \mathbf{p}; t)$. According to our state of knowledge our best predictions for the observables at time t are now given by

$$\Omega_j(t) = \int_\Gamma \rho_0(\mathbf{x}, \mathbf{p}; t) \omega_j(\mathbf{x}, \mathbf{p}; t) \mathrm{d}\Gamma.$$

Using these predicted values as new constraints we derive a new probability density function $\rho(\mathbf{x}, \mathbf{p}; t)$ which maximizes $S(\rho(t))$. It is clear that $S(\rho(t_0)) = S(\rho_0(t_0)) = S(\rho_0(t)) \leq S(\rho(t))$. This approach, even more clearly that does the equilibrium treatment, highlights the fact that entropy is to be regarded, not as an objective property of the system but as dependent upon our knowledge of the system. It is also somewhat more limited that the usual statement of the second law. This can be seen if we consider a number of instances of time later that t_0. Suppose $t_0 < t < t'$. Then using the analysis given above $S(\rho(t_0)) \leq S(\rho(t))$ and $S(\rho(t_0)) \leq S(\rho(t'))$, but we know nothing about the relative sizes of $S(\rho(t))$ and $S(\rho(t'))$. Entropy has not been shown to be monotonically increasing. This aspect of Jaynes' programme was discussed in detail by Lavis and Milligan [32].

6.2 An Objectivist Approach to Non-Equilibrium

The second letter responding to Lebowitz's article in Physics Today is from Driebe [37], a member of Progogine's Brussels-Austin group. His criticism of the Boltzmann/Lebowitz approach is more radical than that of Barnum *et al.* [36]. He makes two points of particular interest for the present discussion: (i) "Irreversibility is not to be found on the level of trajectories or wave-functions, but is instead manifest on the level of probability distributions". (ii) "Many degrees of freedom is not a necessary condition for irreversible behaviour. It is the chaotic dynamics, associated with positive Lyapunov exponents or Poincaré resonances, that causes the system to behave irreversibly". At first sight (i) appears to be simply a restatement of the quote from Sklar, given above, about the need to use, as our element of interest, the probability density function rather than the trajectory. However, I think something more fundamental is implied. Before discussing this question we give a very brief summary of the methods of Prigogine and co-workers.[24]

The subject of interest is the evolution of a set of observable macroscopic quantities, which are taken to be the expectation values $\langle Q_i(t)\rangle$ of phase functions $Q_i(\mathbf{x},\mathbf{p},t)$, $i = 1, 2, \ldots$. Now phase functions corresponding to observables are functions of only a small number of variables,[25] so the probability density function contains a great deal of unwanted detail. The method is to show that, relative to any particular Q_i, the probability density function ρ can be split into two parts $\rho = \rho_1 + \rho_2$, with $\langle Q_i(t)\rangle = \langle Q_i(t)\rangle_1 + \langle Q_i(t)\rangle_2$, so that, the unwanted detail is in ρ_2 with $\langle Q_i(t)\rangle_2$ vanishing identically and $\langle Q_i(t)\rangle_1$ reproducing the unique equilibrium value, corresponding to the thermodynamic quantity, in the limit $t \to \infty$. This procedure can be seen as a "series of successive contractions of the description of a many-body system" [26, p. 689]. For it to work it is necessary that the system has a large number of degrees of freedom and that it satisfies some level of mixing. The latter would certainly be the case if it were a C-system, that is to say chaotic (possesses a positive Lyapunov exponent for almost all initial conditions), [9, p. 262]. This is the point made by Driebe [37].[26] Returning to his comment concerning trajectories and probabilities density functions; it is illuminating to see them in the context of remarks by Prigogine to the effect that we must "eliminate the notion of trajectory from our microscopic description. This actually corresponds to a realistic description: no measurement, no computation leads strictly to a point, to the consideration of a *unique* trajectory. We shall always face a *set* of trajectories", [38, p. 60].[27] I think what is being referred to here is the 'sensitivity to initial conditions' which is present in chaotic systems. This means that, even in principle, we cannot specify the initial conditions with sufficient accuracy to know that the evolution corresponds to the flow along a particular *single* trajectory. However, it seems to me, that there is a conceptual difference between that and the "elimination of the notion of a trajectory".

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[24] For detailed accounts see Prigogine [25] or Balescu [26].

[25] This is the intuition underlying the use of the Boltzmann transport equation and the early terms in the Bogolyubov-Born-Green-Kirkwood-Yvon hierarchy.

[26] His reference to the irrelevance of "many degrees of freedom" is not, I think, a contradiction of Balescu [26, p. 689]. It is certainly the case that some systems with a few degrees of freedom behave irreversibly, but this doesn't mean that they are models for thermodynamic behaviour.

[27] The English translation of this passage is taken from [34].

7 Conclusions

We have seen that programmes for the foundation of statistical mechanics can be based both of subjective and objective views of probability.

The subjective programme, based on the maximum entropy principle of Jaynes, is coherent and mathematically complete. It does, however, have some drawbacks, to which we have referred. (i) Because of it reliance on data collecting it does not seem to be able to take into account non-quantitative information. (ii) Because the probability density function is a property both of the system and our knowledge of the system, thermodynamic quantities, most particularly the entropy, are also properties both of the system and our knowledge of the system. This second point is closely related to the lack of a clear distinction between systems and models of systems.

Objective programmes are much more technically difficult. Equilibrium calculations either rely on some kind of justification for the microcanonical distribution or are the consequence of showing that equilibrium is achieved as the long-time limit from non-equilibrium. The most developed programme for the latter is the work of the Brussels-Austin School which needs the system to be chaotic.

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