

Equilibrium and (Ir)reversibility in Classical Statistical Mechanics*

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1 Introduction

The history of thermometry dates at least from the seventeenth century [1], but the advent of thermodynamics proper can probably be set at the publication by Carnot of his *Réflexions sur la puissance motrice du feu, et sur les machines propres à développer cette puissance*. This work became well-known with its subsequent more analytic reformulation by Clapeyron [2] and inspired the work of Clausius and Kelvin. In the case of each of these the development of thermodynamic concepts was allied to a realization that heat has its origin in the motion of the constituent particles of the system [3], and in the course of the next fifty years the foundations were laid, by Maxwell and Boltzmann (among others), of kinetic theory leading to statistical mechanics. So at least part of the role of statistical mechanics is to provide the explanatory basis for thermodynamics. However, there are difficulties with this, which were known to Maxwell and Boltzmann, and for which there are as yet no universally agreed resolution.

The temporal nature of events in the physical world can be divided into three types, distinguished by thinking of watching them on a film run in both directions. Some happenings appear possible (if eccentric) in both directions; others, like the pieces of a cup rising from the floor and reconstituting themselves into a whole cup strike one as impossible. That leaves a third group of events for which the temporal ordering is less clear. Suppose we have a cup of coffee into which we pour milk. We expect that the milk, starting in one region of the cup, will diffuse into the coffee to form an apparently homogeneous mixture rather than the reverse process. Since there are no obvious forces leading to this outcome it needs an explanation. This is provided by classical thermodynamics which orders equilibrium states according to whether one is adiabatically accessible from the other. The ordering of accessibility of equilibrium states is defined in thermodynamics in terms of the *entropy*. For two equilibrium states X and Y , X is adiabatically accessible from Y only if $S(X) \geq S(Y)$. For the coffee the final state will have larger entropy than the initial state (the increase being the entropy of mixing) and classical thermodynamics, in line

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with common-sense, will assert that the impossibility of the unmixing of the milk and coffee. So what is the problem? More precisely:

- (i) What are the problems in using classical mechanics to produce a microscopic account of thermodynamics?
- (ii) Do the mechanical systems which lead to thermodynamic behaviour have any special features?
- (iii) What are the competing programmes for solving this problem?

We shall describe below the structure of the dynamic models used to represent thermodynamic systems. It is sufficient here to observe that they are normally (a) reversible and (b) volume-preserving. These two distinct properties each conflict with the thermodynamic need for entropy to monotonically increase. The problem posed by having a reversible mechanical system was first noted by Maxwell [4], but brought to Boltzmann's attention in two papers published by Loschmidt [5, 6]. The difficulties posed by volume-preservation are a little more complicated. The most well-known is that the *recurrence theorem* of Poincaré [7] applies [8, p. 214]. Poincaré [9] drew attention to the problem that this posed for kinetic theory, although this was not considered by Boltzmann [10] until it was restated by Zermelo [11]. Less well-known is the problem of the meaning of equilibrium. The 'equilibrium state' of a dynamic system is an *attractor* (stable equilibrium point, stable limit cycle, strange attractor etc.). But volume-preserving systems *do not have attractors* [8, p. 210]; so the concept of (mechanical) equilibrium does not apply to volume-preserving systems. This means that, whatever mechanical description we try to give for thermodynamic equilibrium, it will not be related to the system being in dynamic equilibrium and there will be a need to *define* equilibrium.

Before outlining the different (and conflicting) attempts to resolve these problems it is of interest to give some quotes which indicate where the difficulties lie.

The behaviour of thermodynamic systems, as embodied in the second law of thermodynamics, does not and cannot have an explanation in terms of the microscopic laws of physics *as currently formulated*. (Mackey [12].)

Either there is no temporal asymmetry at any stage, or it is there from the beginning. (Price [13, p. 43].)

Irreversibility is either true on all levels or on none; it cannot emerge as if out of nothing, on going from one level to another. (Prigogine and Stengers [14, p. 285].)

Much of the history that Sklar recounts consists of physicists attempting to continue the programme of deriving the thermodynamic laws from the underlying dynamics even in the face of these objections. What seems odd is the fairly manifest futility of these attempts. (Maudlin [15], in his review of *Physics and Chance* by Sklar [16].)

Sklar [16] in his detailed survey of the foundations of statistical mechanics shows that there is a variety of approaches which can be taken. However, if the dynamic

model is restricted in the way described below, they would seem to be of three main types:

The Weakened Second Law (Typical System) Approach

A vigorous defense of this view has been presented in a sequence of papers by Lebowitz [17, 18, 19]. It can be summed up by the assertion that: “Having results for typical microstates rather than averages is not just a mathematical nicety but at the heart of understanding the microscopic origin of observed macroscopic behaviour.

We neither have nor do we need ensembles when we carry out observations . . . What we do need and can expect is typical behaviour” [17, p. 38]. At the core of this approach is the willingness to accept the consequences of reversibility and recurrence and to modify the weight of the thermodynamic second law to a high probability rather than a certainty. In his reply to Loschmidt [5], Boltzmann [20] argues for this point of view and a similar point is made by Maxwell in his review of Tait’s *Thermodynamics*. He asserts 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, [4, p. 141]. More recently Griffiths [21], Ruelle [22] and Brimont [23] have supported this approach.

The Bayesian (Subjectivist) Approach

Jaynes [24, p. 416]¹ asserts that statistical mechanics “is not a physical theory, but a form of statistical inference”. His maximum entropy method is based on a ‘rational belief’ interpretation of probability which allows the problems posed by reversibility and recurrence to be resolved in a way not open to those who want to produce an ‘objective’ theory. His aim “is not to ‘explain irreversibility’ [in thermodynamics], but to describe and predict the observed facts” [24, p. 416] and he is led to ask the “modest question: ‘Given the partial information that we do, in fact, have, what are the best predictions we can make of observable phenomena?’ ” [24, p. 416]. Whether one is inclined to accept the validity of this approach depends, to a large extent, on being prepared to regard statistical mechanics as simply a procedure for prediction, with the consequent information-related nature of thermodynamic quantities. In particular it means that: “Even at the purely phenomenological level, entropy is an anthropomorphic concept” [24, p. 86].

The Unstable System (Ensemble) Approach

The use of ensembles in statistical mechanics can be traced to the work of Gibbs [26]. However, the reason for their use is not always clear except that they ‘work’. According to Tolman [27, p. 1] the “principles of statistical mechanics are to be regarded as permitting us to make reasonable predictions . . . expected to hold on average . . .”. In more recent times the use of ensembles has acquired, in the view of their proponents, a more intrinsic role. According to Mackey [28, p. 984]: “A thermodynamic system *is* [my italics] a system that has, at any given time, states distributed throughout phase space . . ., and the distribution of these states is characterized by a density . . .”. The density referred to is the ensemble density and thus the ensemble becomes the way that a thermodynamic system is *defined*. According to Prigogine [29, p. 8] “it is at the level of ensembles that temporal evolution can be predicted”. As we shall see the reason for making this assertion is that the subject

¹For convenience references to Jaynes’ work are to his collected papers [24]. For an essay review of this collection see [25].

of statistical mechanics is taken to be unstable systems, for which, according to the Brussels–Austin School [29, 30, 31, 32, 33], it is necessary to develop a ‘complementary’ form of dynamics based on the evolution of a measure density, which is reducible to a trajectory description only when the system is stable.

In the development of statistical mechanics it is customary to argue that the underlying mechanical system has some further special properties beyond those described in the next section. The purpose of these extra restrictions is, of course, to provide a more or less plausible means of overcoming the problems cited above. As to what these extra special features are there is, however, some divergences of view, which roughly divide into three positions, characterized by the following quotes:

- (a) “The specific character of the systems studied in statistical mechanics consists mainly in the *enormous number of degrees of freedom* which these systems possess.” (Khinchin [34, p. 9].)
- (b) The significant feature of a statistical mechanical system is that its “initial state is *incompletely specified*”. (Tolman [27, p. 1].)
- (c) Statistical mechanics is needed when the system is *unstable and therefore chaotic*. “For a stable system we can use a description in terms of trajectories. We can also use a probabilistic description but this leads to a description in terms of trajectories. The statistical description is reducible. On the other hand for chaotic systems the only description which includes the approach to equilibrium is statistical.” (Prigogine [29, p. 60, my translation].)

Of these three propositions the contention that statistical mechanics is about systems with a large number of particles (degrees of freedom) is that with the longest pedigree. It is frequently asserted at the beginning of undergraduate texts [35, p. 140] and the *thermodynamic limit*, where the number of degrees of freedom $N \rightarrow \infty$, is fundamental to many of the exact results in statistical mechanics. A connection between (a) and (b) is often made by the argument that it is the fact that N is large which implies that we are unable to have complete knowledge of the system. While this is true it would go too far for Jaynes. The mere fact that we have incomplete knowledge of the system is sufficient justification for statistical mechanics irrespective of whether $N = 10$ or 10^{23} .² If nevertheless we are interested in arguing that statistical mechanics is a *scientific theory* (not just a procedure for inference) for incompletely specified systems, then we shall want to know why the system is incompletely specified? One possible answer is given by (c). Incomplete knowledge is an intrinsic consequence of *instability* leading to *chaos*. In fact, as is clear from the passage from *Les lois du chaos* cited above, and in other places [36, p. 23], this approach by Prigogine and the Brussels–Austin group takes a more radical position in asserting that in chaotic systems single trajectories *do not exist*.

Many of the fundamental disagreements about the foundations of statistical mechanics can be related to three questions: (i) What does thermodynamics assert?

²For him probabilities, in statistical mechanics and elsewhere, “do not describe reality – only our information about reality” [24, p. 268], the reason for our ignorance about the system is irrelevant.

(ii) What is the meaning of probability? (iii) What kind of mechanics should be used? Their answers to (i) represent the main division between the typical system and ensemble approaches and (ii) represents the main division between the subjectivist approach on the one hand and the typical system and ensemble approaches on the other [37]. The question of the nature of the mechanics used has two levels. The first is more-or-less benign in the sense that it would be common to all three approaches. The second represents the ‘heavier duty’ properties (ergodic, mixing, chaotic etc.) which are judged to be important by the Brussels–Austin Group, irrelevant by Jaynes’ group and of limited significance for the analysis of typical systems.³

1.1 The Dynamics

We now describe briefly the dynamic system assumed to be used for statistical mechanics. We have a microstructure represented by an N -dimensional vector \mathbf{x} in a phase space Γ_N . Some dynamics $\mathbf{x} \rightarrow \phi_t \mathbf{x}$, ($t \geq 0$) determines a *flow* in Γ_N and the set of points $\mathbf{x}(t) = \phi_t \mathbf{x}(0)$, parameterized by $t \geq 0$, gives a *trajectory*.⁴ There is a measure on Γ_N given by an $\mathcal{L}^{(1)}$ density $\rho(\mathbf{x}; t)$. We suppose that the system is (a) classical, (b) finite, (c) deterministic,⁵ (d) autonomous. A consequence of (d) is that the operators $\{\phi_t\}_{t \geq 0}$ form a semi-group. Let the time-evolution of the system be determined by the equation of motion $\dot{\mathbf{x}}(t) = \mathbf{F}(\mathbf{x})$. Then a constant of motion $f(\mathbf{x}; t)$, and a measure density $\rho(\mathbf{x}; t)$, which yields an invariant measure on Γ_N , satisfy

$$\frac{\partial f}{\partial t} + \mathbf{F} \cdot \nabla(f) = 0 \quad \text{and} \quad \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{F}) = 0, \quad (1)$$

respectively, the latter being *Liouville’s equation*. The two remaining properties of interest will now be defined:

- (e) The system is *reversible* if there exists an operator J on the points of Γ_N , such that $\phi_t \mathbf{x} = \mathbf{x}'$ implies $J^{-1} \phi_t J \mathbf{x}' = \mathbf{x}$. Then $\phi_{-t} = J^{-1} \phi_t J$ and the set $\{\phi_t\}_{t \in \mathbb{R}}$ is a *group*.⁶
- (f) Measure is preserved by the flow if ρ satisfies Liouville’s equation. *This is a restriction on ρ not the system*. A system is *volume-preserving* if Liouville’s equation is satisfied by $\rho = 1$; then $\nabla \cdot \mathbf{F} = 0$. *This is a restriction on the system*.

Not all reversible systems are volume-preserving and not all volume-preserving systems are reversible. For a volume-preserving system the equations (1) take the same form; so *an invariant measure density is a constant of motion*.⁷

³Lebowitz seems to waver a little on the need for ergodicity.

⁴We are primarily interested in the case where both t and Γ_N are continuous and our discussion will be expressed in this form. However, it is often necessary for investigative purposes to use examples where one or both of these is discrete [38].

⁵Although stochastic examples can often be heuristically useful [38].

⁶For an ‘ordinary’ dynamic system, the variables \mathbf{x} are divided into conjugate configuration \mathbf{q} and momentum \mathbf{p} variables with $J(\mathbf{q}, \mathbf{p}) = (\mathbf{q}, -\mathbf{p})$.

⁷An autonomous reversible *Hamiltonian system* is a special case of a volume-preserving system. The Hamiltonian is a constant of motion and energy hyper-surfaces are invariant sets in Γ_N .

Let $\Sigma \subset \Gamma_N$ be invariant with respect to the ϕ_t and let $\rho(\mathbf{x}; t)$ be normalized over Σ . The functional

$$S_G(\rho; t) = -k_B \int_{\Sigma} \rho(\mathbf{x}; t) \ln\{\rho(\mathbf{x}; t)\} d^N x, \quad (2)$$

where k_B is *Boltzmann's constant*, is the Gibbs entropy.⁸ If $\rho(\mathbf{x}; t)$ satisfies Liouville's equation then $S_G(\rho; t)$ is constant (with respect to time).⁹

We now define some of the more specialized properties of dynamic systems, which have been regarded as significant for statistical mechanics. Let $\Sigma \subset \Gamma_N$ be invariant with respect to ϕ_t and $\langle f \rangle_{\sigma}$ denote the integral of f over $\sigma \subseteq \Sigma$. Then the system is:

Ergodic if Σ has no non-trivial invariant subsets. Then the following results can be established:

- (i) The time-independent solution $\rho^*(\mathbf{x})$ to Liouville's equation, is unique to within normalization and an additive u such that $\langle u \rangle_{\Sigma} = 0$. We shall, as a convenient name,¹⁰ call $\rho^*(\mathbf{x})$, with $\langle \rho^* \rangle_{\Sigma} = 1$, the *equilibrium density function*.
- (ii) The infinite time average along a trajectory of a phase function $f(\mathbf{x})$ is equal to its phase average $\langle f \rho^* \rangle_{\Sigma}$.
- (iii) With $\sigma \subset \Sigma$ of non-zero measure, $\lim_{\tau \rightarrow \infty} \frac{T(\sigma; \tau)}{\tau} = \langle \rho^* \rangle_{\sigma} = \mathcal{M}^*(\sigma)$, where $T(\sigma; \tau)$ is the time during the interval $[0, \tau]$ in which the trajectory is in σ . This must, of course, be infinite as $\tau \rightarrow \infty$ for the limit to be non-zero.¹¹

The simple harmonic oscillator is ergodic.

Mixing if the following condition holds. Let $\alpha, \gamma \subset \Sigma$ and let \mathcal{M}^* be an invariant equilibrium measure on Σ . If, in the infinite time limit, the part of the mapping of γ which is in α is, in measure, proportional to the size of γ relative to the whole of Σ then the system is mixing. A mixing flow is ergodic (but not the converse) and the equilibrium measure used in the definition is unique. The simple harmonic oscillator is not mixing.

Kolmogorov (a K-system) if it admits of a K-partition of Σ .¹² K-systems are mixing. In 1963 Sinai proved that a system of more than two hard spheres in a cube with perfectly reflecting walls is a K-system [41].

⁸At the moment this is just a convenient name without any physical baggage.

⁹This result is not dependent on the system being volume-preserving.

¹⁰Without implying any specific meaning for the word 'equilibrium'.

¹¹It follows from the Poincaré recurrence theorem the trajectory must keep returning to points arbitrarily close to $\mathbf{x} \notin \sigma$. It must therefore pass through σ an infinite number of times.

¹²The rather technical definition of this is given in [39, p. 32] and [40, p. 80].

Bernoulli if there is a Bernoulli-partition B_n of Σ . This is defined in the following way. Let B_n be a partition of Σ into n subsets. Label the members of B_n with the integers $[0, 1, \dots, n-1]$ and, for any trajectory and some Δt , record the infinite sequence of numbers $\mathcal{S} = \{\dots, s_{-2}, s_{-1}, s_0, s_1, s_2, \dots\}$, where the trajectory is in the set b_{s_k} labelled s_k at time $k\Delta t$. The partition is Bernoulli if all sequences \mathcal{S} are uncorrelated and no two distinct trajectories have the same sequence. A Bernoulli system is a K-system. The most celebrated example of a Bernoulli system is the *baker's transformation* (see below).

Exact if, for all $\sigma \subset \Sigma$, of non-zero measure, $\lim_{t \rightarrow \infty} \mathcal{M}^*(\phi_t \sigma) = 1$. Such a system cannot be reversible but it will be ergodic and mixing with a unique equilibrium measure $\rho^*(\mathbf{x})$, and any invariant measure density $\rho(\mathbf{x}; t)$ satisfies

$$\lim_{t \rightarrow \infty} \rho(\mathbf{x}; t) = \rho^*(\mathbf{x}). \quad (3)$$

The missing member in this taxonomy is **chaotic**. This is rarely defined, even in books for which ‘chaos’ features in the title [8, 40]. A possible definition could be given in terms of the *Lyapunov exponents* of the flow [8, p. 129–138]. Roughly speaking a positive or negative Lyapunov exponent corresponds respectively to a dilation or contraction of volume, with the flow, in that direction. A system is *chaotic* if it has at least one positive Lyapunov exponent and the sum of the exponents is not positive. For any system to have an attractor (probably strange in a chaotic system) the sum of its Lyapunov exponents must be negative. As we have already noted volume-preserving flows (including Hamiltonian systems) do not have attractors and the sum of their Lyapunov exponents is zero. K-systems are chaotic; some mixing systems which are not K-systems are also chaotic.

2 The Weakened Second Law Approach

This approach is based on an explicit initial distinction between the micro and macro levels. Consider a system, which at time t has microstate given by $\mathbf{x}(t) \in \Gamma_N$. Macrostates (observable states) are defined by a set Ξ of macroscopic variables.¹³ Let the set of macrostates be $\{\mu\}_\Xi$. They are so defined that every $\mathbf{x} \in \Gamma_N$ is in exactly one macrostate denoted by $\mu(\mathbf{x})$ and the mapping $\mathbf{x} \rightarrow \mu(\mathbf{x})$ is many-one. Every macrostate μ is associated with its ‘volume’ $\mathcal{V}(\mu) = \mathcal{V}_\mu$ in Γ_N .¹⁴ We thus have the map $\mathbf{x} \rightarrow \mu(\mathbf{x}) \rightarrow \mathcal{V}_\mu(\mathbf{x})$ from Γ_N to \mathfrak{R}^+ or the positive integers. The *Boltzmann entropy* is defined by

$$S_B(\mathbf{x}) = k_B \ln[\mathcal{V}_\mu(\mathbf{x})]. \quad (4)$$

This is a phase function depending on the choice of macroscopic variables Ξ . How do we expect that it will behave? The point of view of this approach can be expressed as follows:

¹³These may include some thermodynamic variables (volume, number of particles etc.) but they can also include other variables, specifying, for example, the number of particles in a set of subvolumes. Ridderbos [42] denotes these by the collective name of *supra-thermodynamic variables*.

¹⁴In the case where Γ_N is continuous the volume of μ will normally be its Lebesgue measure; when Γ_N is discrete the volume will be the number of points in μ .

If the system starts at a phase point with low entropy then we expect the entropy to increase. As it increases there will be fluctuations, which could be large. When the entropy gets near to its maximum value then it will still fluctuate with possibly large fluctuations to small entropy values, but we don't expect these to occur very often.

This, of course, runs counter to the strict form of the second law, which does not allow any decreases in entropy of an isolated system. Before discussing this we consider the simple example of a gas of particles moving under the action of the *baker's transformation*.¹⁵ This transformation is as shown in Fig. 1, where a unit square is stretched to twice its width and then cut in half with the right-hand half used to restore the upper half of the unit square. As a mapping ϕ on the cartesian coordinates (x, y) of the unit square it is given by

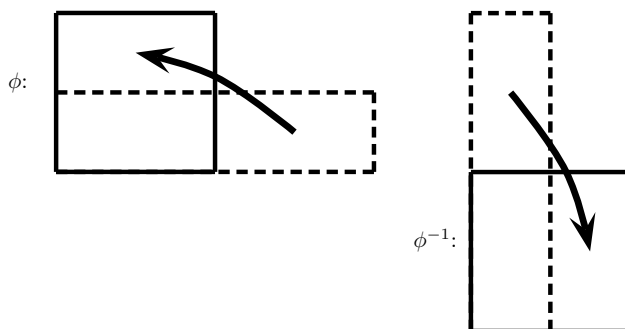


Figure 1: The baker's transformation and its inverse.

$$\phi(x, y) = \begin{cases} (2x, \frac{1}{2}y), & \text{mod } 1, & 0 \leq x < \frac{1}{2}, \\ (2x, \frac{1}{2}(y+1)), & \text{mod } 1, & \frac{1}{2} \leq x < 1. \end{cases} \quad (5)$$

One way of writing this transformation is to express x and y as binary strings:

$$x = 0 \cdot x_1 x_2 x_3 \dots, \quad y = 0 \cdot y_1 y_2 y_3 \dots, \quad (6)$$

where x_j and y_j take the values 0 or 1. Then the transformation can be represented by writing the digits for the initial point as $\dots y_5 y_4 y_3 y_2 y_1 | x_1 x_2 x_3 x_4 x_5 \dots$ and ϕ and ϕ^{-1} correspond respectively to moving the vertical bar one step to the right and left.¹⁶ It can be shown [40, p. 54–56] that the baker's transformation is volume-preserving and thus that the Poincaré recurrence theorem applies. Now suppose that a trajectory starts at a randomly chosen point in the small square $0 \leq x < 2^{-m}$, $0 \leq y < 2^{-m}$. This simply means that in the binary string there are m entries of zero on each side of the bar. The trajectory will return to the square when, after

¹⁵A collection of other examples can be found in [38].

¹⁶ $\phi^{-1} = J\phi J$ where $J(x, y) = (y, x)$.

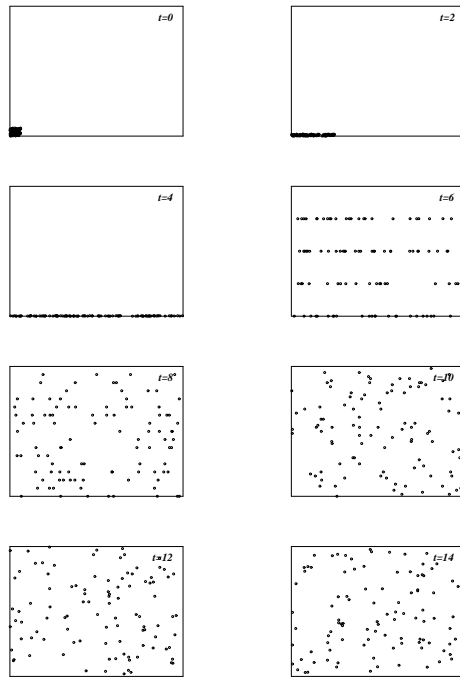


Figure 2: A gas of $N = 50$ particles moving under the baker's transformation.

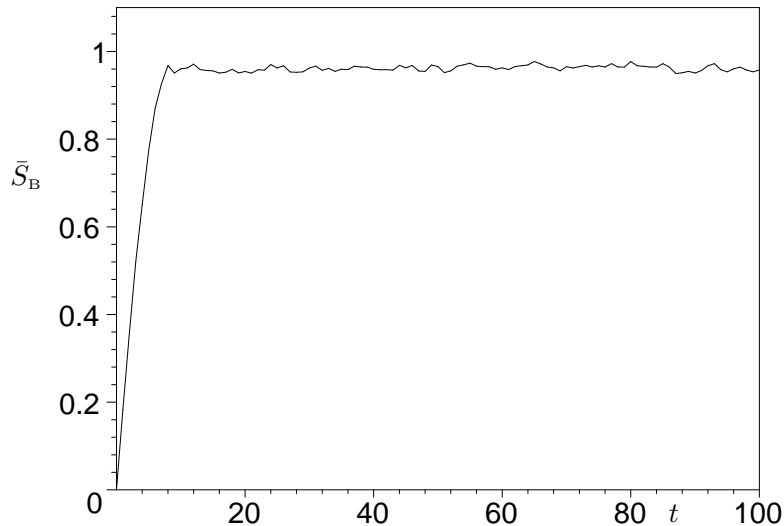


Figure 3: The evolution of the Boltzmann entropy for a gas of $N = 50$ particles moving under the baker's transformation.

some translations of the bar, this again happens. The mean first recurrence time is 2^{2m} steps [38] and it is not difficult to show that the baker's transformation is Bernoulli [38].

But as indicated above, we are actually interested in the application of the baker's transformation to a 'gas' of N points (a *baker's gas*). We start all the points in some small subset of the unit square and watch them evolve. Suppose the square is divided into 2^{2m} equal square cells and all the particles begin in the bottom left-hand cell. Fig. 2 shows the evolution for a gas of $N = 50$ particles with $m = 4$ (256 cells). Now we suppose that the macrostates correspond to identifying the number of particles N_{ij} in each of the cells $i, j = 1, 2, \dots, 2^m$. Then

$$\mathcal{V}(\{N_{ij}\}) = \frac{N!}{\prod_{i,j} N_{ij}!}, \quad (7)$$

and Fig. 3 shows the evolution of the Boltzmann entropy. The entropy will return to its initial value if all the particles arrive in the same cell. The mean time for this to occur is $2^{2m(N-1)}$ [38]. For $m = 4$, $N = 50$ this approximates to 10^{118} steps.

The problem with this approach to irreversibility and equilibrium is the absence of rigorous results. The best that can be done is to investigate simple models using both simulations and model-specific calculations. Based on this the following conclusions can be suggested:

- Experiments with stochastic models show that thermodynamic-type behaviour needs there to be some smoothness in the entropy changes which

occur as the trajectory passes from one macrostate to the next. This implies some restrictions of accessibility between macrostates. This is normally achieved by the dynamics and a reasonable choice of macrostate structure.

- Given a macrostate μ of volume $\mathcal{V}(\mu)$, let $v^{(\pm)}(\mu)$ be the proportions in terms of total volume of the macrostates accessible from μ which have volumes [larger or equal]/[smaller] than $\mathcal{V}(\mu)$. In models where the calculation can be made we have shown [38] that $v^{(\pm)}(\mu)$ converge monotonically above/below to $\frac{1}{2}$ as \mathcal{V} tends towards the macrostate of largest volume \mathcal{V}_{\max} .¹⁷ This suggests that when $\mathcal{V}(\mu) \ll \mathcal{V}_{\max}$ a typical trajectory will pass into a macrostate of larger volume. *Entropy will typically increase.* When $\mathcal{V}(\mu) \doteq \mathcal{V}_{\max}$ a typical trajectory will pass into macrostates of larger or smaller volume with almost equal probabilities. *Entropy will fluctuate.* Large fluctuations downwards from the maximum volume/entropy will be rare. To achieve a large reduction of entropy find a trajectory which has recently come from a state of low entropy and reverse it. This will, if it can be done exactly, achieve untypical behaviour.

3 The Bayesian Approach

The argument from this standpoint which leads to an increasing entropy is given by Jaynes [24, p. 27]. The basis of Jaynes' method is to ask what is the best probability distribution to use for the system given the information that we have. 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 the unique measure of uncertainty, which satisfies some reasonable mathematical properties, is Shannon's *information entropy* which, for the dynamic system described in Sect. 1.1, is (to within a constant) the Gibbs entropy (2). 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). The way that this is realized is discussed in detail by Lavis and Milligan [25] and in the author's contribution to the previous symposium in this series [37]. A brief summary is as follows. Suppose we have the time-dependent observables $\{\Omega_j(t)\}$ related to phase functions $\{\omega_j(\mathbf{x}; t)\}$ by $\Omega_j(t) = \langle \omega_j(t) \rho(t) \rangle$. Measurements are made of these observables at the time t_0 with the results $\{\bar{\Omega}_j(t_0)\}$. The probability density function $\rho(\mathbf{x}; t_0) = \rho_0(\mathbf{x}; t_0)$ is the one which maximizes $S_G(\rho; t_0)$ subject to the constraints $\bar{\Omega}_j(t_0) = \langle \omega_j(t_0) \rho(t_0) \rangle$. The probability density function evolves according to Liouville's equation (1) and at a later time t is given by $\rho_0(\mathbf{x}; t)$. According to our state of knowledge our best predictions for the observables at time t are now given by $\Omega_j(t) = \langle \omega_j(t) \rho_0(t) \rangle$. Using these predicted values as new constraints we derive a new $\rho(\mathbf{x}; t)$ which maximizes $S_G(\rho; t)$. It is clear that $S_G(\rho; t_0) = S_G(\rho_0; t_0) = S_G(\rho_0; t) \leq S_G(\rho; t)$. This approach highlights, even

¹⁷Of course, if μ is the unique macrostate of largest volume $v^{(+)}(\mu) = 0$, $v^{(-)}(\mu) = 1$.

more clearly that does Jaynes' equilibrium treatment, 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 in that it does not establish that entropy is monotonically increasing, but merely that it is larger at any time when it is recalculated.

4 The Unstable System Approach

For a reversible volume-preserving system, as described in Sect. 1.1, let $\Sigma \subset \Gamma_N$ be invariant under the flow ϕ_t . Reversibility implies that the operators $\{\phi_t\}_{t \in \mathbb{R}}$ form a group and volume-preservation means that the Frobenius-Perron operators $\{U_t\}_{t \in \mathbb{R}}$, given by

$$U_t \rho(\mathbf{x}; 0) = \rho(\phi_{-t}(\mathbf{x}); 0) = \rho(\mathbf{x}; t), \quad (8)$$

are unitary and also form a group with their inverses given by the corresponding Koopman operators [40].

In the ensemble approach equilibrium is *defined* to be the state described by a time-independent solution $\rho^*(\mathbf{x})$ of Liouville's equation.¹⁸ As was indicated in Sect. 1.1, for an ergodic system $\rho^*(\mathbf{x})$ exists and is unique. But for any arbitrary solution $\rho(\mathbf{x}; t)$ of Liouville's equation to satisfy (3) and converge to the unique equilibrium solution the system must be *exact* [40]. However, an exact system is not reversible, and this is the fundamental problem for which the Brussels–Austin group propose a solution. The evolution of their work from the late-sixties to the present has been described in detail by Edens [43]. He divides the work into periods, the early years (1969–1985) and the later years (1988–present). In the former three strands can be distinguished: (a) subdynamics, [30]; (b) Λ -transformations, [31, 36, 44]; (c) entropy as a selector of initial conditions, [45]. In our brief treatment of this work we shall concentrate of the later part of this period.

Let $\varpi(\mathbf{x}; \gamma; t)$ be the probability of a transition from $\mathbf{x} \in \Sigma$ to a point in $\gamma \subset \Sigma$ in time t and define the family of operators $\{W_t\}_{t \in \mathbb{R}^+}$ by

$$W_t f(\mathbf{x}) = \int_{\Sigma} f(\mathbf{x}') \varpi(\mathbf{x}; d^N x'; t), \quad \forall f \in \mathcal{L}^{(2)}. \quad (9)$$

It can be shown [31] that, if $\varpi(\mathbf{x}; \gamma; t)$ is a Markov process, then $\{W_t\}_{t \in \mathbb{R}^+}$ is a semi-group which preserves positivity and under which the uniform density is invariant.¹⁹ The next step is to find a non-unitary operator Λ so that

$$\Lambda U_t = W_t^\dagger \Lambda, \quad \text{and for which, we define } \dot{\rho}(\mathbf{x}; t) = \Lambda \rho(\mathbf{x}; t). \quad (10)$$

Then it follows from (8) and (10) that

$$W_t^\dagger \dot{\rho}(\mathbf{x}; 0) = \dot{\rho}(\mathbf{x}; t). \quad (11)$$

Now it is necessary to determine the class of systems for which Λ exists, preserves positivity, the equilibrium density and the measure of any $\gamma \subset \Sigma$. We also want

¹⁸Hence the title 'equilibrium density function' coined on page 7.

¹⁹Since the systems under consideration are *at least* ergodic the uniform density either is, or induces, the unique equilibrium density.

$\|W_t^\dagger \hat{\rho} - \rho^*\|^2$ to decrease strictly monotonically to zero as $t \rightarrow +\infty$. However, when this is true there is another subgroup $\{W_t'\}_{t \in \mathbb{R}^-}$ which shows the convergence when $t \rightarrow -\infty$. So the problem is in two parts, first to find the non-unitary operator Λ and then to give some principle which distinguishes between the realization which shows ‘thermodynamic behaviour’ as $t \rightarrow +\infty$ and that for which this occurs as $t \rightarrow -\infty$. One possible approach, for a K-system, is to course-grain onto a K-partition [44]. This means that Λ is a projection and does not have an inverse. The two representations are not complementary and there is a loss of information. The density $\rho(\mathbf{x}; t)$ cannot be reconstructed from the course-grained $\hat{\rho}(\mathbf{x}; t)$. An alternative procedure for K-systems can be developed [46, 47] in which Λ is invertible. However, “reconstruction is not possible for arbitrarily large time except if one assumes infinite accuracy in the observation of the physically evolving states” [46, p. 425]. The question of distinguishing between thermodynamic and non-thermodynamic time evolution is treated by Courbage [47]. The details are technical, but the idea is to use entropy as a measure of the information needed to construct the initial state of the system. Non-thermodynamic behaviour needs the provision of an infinite amount of information. This idea has a more than superficial similarity to the trick, in the weakened second law approach, of achieving large Boltzmann entropy decreases in computer experiments by reversing the trajectory.

5 Conclusions

We have discussed three approaches²⁰ to statistical mechanics which imply radically different meaning for irreversibility and equilibrium.

In the *weakened second law approach* the entropy is a phase function along a trajectory given by a combination of the dynamics and macrostate structure of the system. In consequence it fluctuates, but the dynamics and macrostate structure combine to ensure that the fluctuations are typically small when the entropy is close to its maximum. This entropy maximum is identified with the system being in its macrostate of maximum volume which is *defined* to be the equilibrium state. A steep entropy increase occurs only when the system starts far from equilibrium in a macrostate of small volume.

In the *baysian approach* entropy is a measure of uncertainty about the system. At any time it is calculated by finding the probability distribution which best represents our information about the system. Equilibrium is simply the state in which our information is time-independent. If the information changes with time, and we make no attempt to update it, it will necessarily become out-of-date, that is decrease, and thus entropy will be larger when it is recalculated using this information. This is an approach which is mathematically faultless, however, you must be prepared to accept the anthropomorphic nature of entropy.

The *unstable system approach* takes as its starting point the supposition that thermodynamic behaviour is an ensemble property. Classically this would have implied that we were dealing, not with a single system, but an average over a collection (ensemble) of systems. This would seem not to be the intention of Prigogine and

²⁰There are other approaches (for a survey see e.g. Sklar [16]) which space does not allow us to consider. In particular the *deus ex machina* approach in which irreversibility arises from outside interference is quite popular.

his group. Their aim is to develop a new form of dynamics which contains both the usual dynamic description based on trajectories and a thermodynamic description based on ensembles. These will be “*complementary* descriptions analogous to the ‘complementarity’ encountered in quantum mechanics” [33]. The ensemble description will be reducible to the trajectory description only when the system is not chaotic. This project serves to support the contention of Mackey (quoted on page 3) that a new form of mechanics is needed to produce a statistical mechanics which yields monotonic entropy increase. However, the conceptual content of the assertion that the *sole* description of a chaotic system is in terms of a distribution is less clear. The reference to an analogy with quantum mechanics might lead one to suppose that some kind of ‘no-hidden-variable’ demonstration is necessary [48]. The only form of this which is provided is the demonstration [49] that even when $\rho(\mathbf{x}; t)$ is localized in a region, however small, $\dot{\rho}(\mathbf{x}; t)$ will be spread over all the accessible set $\Sigma \subset \Gamma_N$. This seems to be less than a proof of the non-existence of trajectories.

References

- [1] G. Emch and C. Liu. *The logic of thermostistical physics*. Springer, 2002.
- [2] B. P. Clapeyron. Mémoire sur la puissance motrice de la chaleur. *J. Ecole Polytechnique*, XIV, 23:153–190, 1834.
- [3] R. Clausius. The nature of the motion which we call heat. Reprinted in Brush [50] Vol. 1, pages 111–134, 1857.
- [4] P. M. Harman. *The natural philosophy of James Clerk Maxwell*. Cambridge U. P., 1998.
- [5] J. Loschmidt. *Wiener Beri.*, 73:139, 1876.
- [6] J. Loschmidt. *Wiener Beri.*, 75:67, 1877.
- [7] H. Poincaré. On the three-body problem and the equations of dynamics. Reprinted in Brush [50], Vol. 2, pages 194–202, 1890.
- [8] E. Ott. *Chaos in dynamical systems*. Cambridge U. P., 1993.
- [9] H. Poincaré. Mechanism and experience. Reprinted in Brush [50], Vol. 2, pages 203–207, 1893.
- [10] L. Boltzmann. Reply to Zermelo’s remarks on the theory of heat. Reprinted in Brush [50], Vol. 2, pages 218–228, 1896.
- [11] E. Zermelo. On a theorem of dynamics and the mechanical theory of heat. Reprinted in Brush [50], Vol. 2, pages 208–217, 1896.
- [12] M. C. Mackey. Microscopic dynamics and the second law of thermodynamics. In C. Mugnai, A. Ranfagni, and L. S. Schulman, editors, *Time’s arrows, quantum measurement and superluminal behaviour*, pages 49–65. Consiglio Nazionale Dell Ricerche, Roma, 2001.

- [13] H. Price. *Time's arrow and Archimedes' point: new directions for the physics of time*. Oxford U. P., 1996.
- [14] I. Prigogine and I. Stengers. *Order out of chaos*. Heinemann, 1984.
- [15] T. Maudlin. Review of Sklar [16]. *Brit. J. Phil. Sci.*, 46:45–149, 1995.
- [16] L. Sklar. *Physics and chance*. Cambridge U. P., 1993.
- [17] J. L. Lebowitz. Boltzmann's entropy and time's arrow. *Physics Today*, 46:32–38, September 1993.
- [18] J. L. Lebowitz. Time's arrow and Boltzmann's entropy. In J. J. Halliwell, J. Pérez-Mercader, and W. H. Zurek, editors. *Physical origins of time asymmetry*. page 131, Cambridge U. P., 1994.
- [19] J. L. Lebowitz. Statistical mechanics: A selective review of two central issues. *Rev. Mod. Phys.*, 71:S386–S357, 1999.
- [20] L. Boltzmann. On the relation of a general mechanical theorem to the second law of thermodynamics. Reprinted in Brush [50], Vol. 2, pages 188–193, 1877.
- [21] R. B. Griffiths. Statistical irreversibility: classical and quantum. In J. J. Halliwell, J. Pérez-Mercader, and W. H. Zurek, editors. *Physical origins of time asymmetry*. page 147, Cambridge U. P., 1994.
- [22] D. Ruelle. *Chance and chaos*. Princeton U. P., 1991.
- [23] J. Bricmont. Science of chaos or chaos in science? *Physica*, 17:159–208, 1995.
- [24] E. T. Jaynes. *Papers on probability, statistics and statistical physics*. Reidel, 1983. Edited by Rosenkratz, R. D.
- [25] D. A. Lavis and P. J. Milligan. The work of E. T. Jaynes on probability, statistics and statistical physics. *Brit. J. Phil. Sci.*, 36:193–210, 1985.
- [26] J. W. Gibbs. *Elementary principles in statistical mechanics*. Yale U. P., 1902. Reprinted by Dover Publications, 1960.
- [27] R. C. Tolman. *The principles of statistical mechanics*. Oxford U. P., 1938.
- [28] M. C. Mackey. The dynamic origin of increasing entropy. *Rev. Mod. Phys.*, 61:981–1015, 1989.
- [29] I. Prigogine. *Les lois du chaos*. Flammarion, 1994.
- [30] R. Balescu. *Equilibrium and non-equilibrium statistical mechanics*. Wiley, 1975.
- [31] B. Misra, I. Prigogine, and M. Courbage. From deterministic dynamics to probabilistic descriptions. *Physica A*, 98:1–26, 1979.
- [32] I. Prigogine. Laws of nature, probability and time symmetry breaking. *Physica A*, 263:528–539, 1999.

- [33] B. Misra. Nonequilibrium entropy, Lyapounov variables and ergodic properties of classical systems. *Proc. Natl. Acad. Sci. USA*, 75:1627–1631, 1978.
- [34] A. I. Khinchin. *Mathematical foundations of statistical mechanics*. Dover, 1949.
- [35] K. Huang. *Statistical mechanics*. John Wiley, 1963.
- [36] B. Misra and I. Prigogine. Time, probability and dynamics. In C.W. Horton, Reichl L. E., and V. G. Szebehely, editors, *Proceedings of the workshop on long-time predictions in nonlinear conservative dynamical systems*, pages 21–43. Wiley, 1981.
- [37] D. A. Lavis. The concept of probability in statistical mechanics. In B. G. Sidharth and M. V. Altaisky, editors, *Frontiers of Fundamental Physics, 4*, pages 293–308. Kluwer, 2001.
- [38] D. A. Lavis. Some examples of simple systems. Available at: www.mth.kcl.ac.uk/~dlavis/papers/examples.pdf, 2002.
- [39] V. I. Arnold and A. Avez. *Ergodic problems of classical mechanics*. Benjamin, 1968.
- [40] A. L. Lasota and M. C. Mackey. *Chaos, fractals and noise*. Springer, 1994.
- [41] Ja. G. Sinai. Ergodicity of Boltzmann’s gas model. In T. H. Bak, editor, *Statistical mechanics: foundations and applications*, pages 559–573. Benjamin, 1967.
- [42] K. Ridderbos. The course-graining approach to statistical mechanics: how blissful is our ignorance? *Stud. Hist. Phil. Mod. Phys.*, 33:65–77, 2002.
- [43] B. Edens. *Semigroups and symmetry: an investigation of Prigogine’s theories*. PhD thesis, Institute for History and Foundations of Science, Utrecht University, 2001. Available at: <http://philsci-archive.pitt.edu/documents/disk0/00/00/04/36/>.
- [44] B. Misra and I. Prigogine. On the foundations of kinetic theory. *Sup. Prog. Theor. Phys.*, 69:101–110, 1980.
- [45] M. Courbage and I. Prigogine. Intrinsic randomness and intrinsic irreversibility in classical dynamical systems. *Proc. Natl. Acad. Sci. USA*, 80:2412–2416, 1983.
- [46] B. Misra and I. Prigogine. Irreversibility and nonlocality. *Let. Math. Phys.*, 7:421–429, 1983.
- [47] M. Courbage. Intrinsic irreversibility of Kolmogorov dynamical systems. *Physica A*, 122:459–482, 1983.
- [48] R. W. Batterman. Randomness and probability in dynamical theories: on the proposals of the Prigogine school. *Philosophy of Science*, 58:241–262, 1991.
- [49] S. Goldstein, B. Misra, and M. Courbage. On intrinsic randomness of dynamical systems. *J. Stat. Phys.*, 25:111–126, 1981.
- [50] S. G. Brush. *Kinetic theory*, Vol. 1, Pergamon, 1965; Vol. 2, Pergamon, 1966.