Abstract

Boltzmann’s struggle with a derivation of the Second Law of Thermodynamics is sketched. So is his first derivation of the connection between entropy and probability in 1877. Planck’s derivation and quantum mechanical modifications of Boltzmann’s connection between entropy probability are given next. Then Einstein’s objections to a purely probabilistic rather than a dynamical interpretation of entropy are discussed. Finally, the dynamical basis of the Sinai-Ruelle-Bowen distribution for very chaotic systems is sketched and appears to be an example of Einstein’s dynamical interpretation of entropy.

I. Introduction

Boltzmann had a strong disposition for mechanics and his first papers were all devoted to purely mechanical derivations of the Second Law of Thermodynamics. The most important one was that based on the 1872 Boltzmann equation, i.e. on the dynamics of binary collisions, where he says at the end:

“One has therefore rigorously proved that, whatever the distribution of the kinetic energy at the initial time might have been, it will, after a very long time, always necessarily approach that found by Maxwell”\[1\].

He seems to have overlooked entirely that the Stoszahl Ansatz, i.e. the assumption of molecular chaos used in his equation, was a statistical assumption which had no dynamical basis.

It is therefore, in my opinion, ironic that perhaps his most famous achievement may well have been the relation of 1877 between entropy and probability, which was devoid of any dynamical feature\[2\].
Whenever later dynamical results were obtained, e.g. by Helmholtz, when he introduced his monocyclus in 1884\cite{3}, Boltzmann immediately jumped at it and extended it to what we now call the origins of ergodic theory, i.e. a dynamical theory\cite{4}. Also his summarizing lectures in the two volume “Lectures on Gas Theory”\cite{5} mostly discuss dynamical approaches and reference to the entropy-probability relation can mainly be found on a few pages of the first book in connection with the statistical interpretation of his $H$-function (ref.5,1,p.38).

However, in this lecture I do want to concentrate on his work on entropy and probability first and end with a revival of the dynamical approach as proposed by Einstein and as later used, in my view, in the dynamical approach to phase space probabilities in the Sinai-Ruelle-Bowen (SRB) distribution. The sudden switch which Boltzmann made from a purely dynamical to a purely probabilistic approach, might well have been due to the critical attacks of many of his colleagues on the Stoszzahl Ansatz, as exemplified by Loschmidt’s Reversibility Paradox\cite{6a} and Zermelo’s Recurrence Paradox\cite{6b}.

II. Boltzmann’s original derivation of $S \sim \log W$

This was done in a paper of 1887\cite{2}: “On the relation between the Second Law of the Mechanical Theory of Heat and Probability Theory with respect to the laws of thermal equilibrium.” I will sketch first the simplified procedure Boltzmann follows in Chapter I of this paper.

The crucial statement here is: “For an ideal gas in thermal equilibrium the probability of the number of “complexions” of the system is a maximum.”

Boltzmann introduced the notion of “complexions” as follows:

a) Assume discrete kinetic energy values of each molecule, which are represented in an arithmetic series:

$$\varepsilon, 2\varepsilon, 3\varepsilon, ..., p\varepsilon,$$

where each molecule can only have a finite number, $p$, of kinetic energies $\varepsilon$.

b) Before each binary collision the total kinetic energy of the two colliding molecules is always contained in the above series and “by whatever cause” the same is true after the collision. He says:

“There is no real mechanical system [to which this collision assumption is applicable], but the so-defined problem is mathematically much easier to deal with and [in addition] it goes over in the problem we want to solve, when the kinetic energies of the molecules become continuous and $p \rightarrow \infty$.”
Assume that the possible kinetic energies of the $N$ molecules are distributed in all possible ways at constant total kinetic energy $E$. Then each such distribution of the total kinetic energy over the molecules is called a complexion. What is the number $P$ of complexions, where $w_j$ molecules possess a kinetic energy $j\varepsilon$ ($j = 1, \ldots, N$)? This number $P$ [which Boltzmann calls “the permutability” or “thermodynamic probability”] indicates how many complexions correspond to a given molecular distribution or state of the system. A distribution can be represented by writing down first as many $j$’s as there are molecules with a kinetic energy $j\varepsilon$ ($w_j$) etc. Obviously $P = N!/\Pi_{j=1}^p w_j!$. The most probable distribution is that for which the \{w_j\} are such that $P = \max$ or $\Pi_{j=1}^p w_j!$ or also $\log \Pi_{j=1}^p w_j!$ a minimum. With the constraints $\sum_{j=1}^p w_j = N$ and $\sum_{j=1}^p (j\varepsilon)w_j = E$ and Stirling’s approximation, Boltzmann finds then for the probability that the kinetic energy of a molecule is $s\varepsilon$:

$$w_s \sim -\exp -s\varepsilon/\bar{\varepsilon}$$

with $\bar{\varepsilon} = \frac{E}{N}$, the average kinetic energy of a molecule.

Boltzmann adds that: “in order to translate the above [derivation] into the mechanical theory of heat, in particular into the introduction of differentials [when one makes the kinetic energies of the molecules continuous rather than discrete], needs still some thought and a not unimportant modification of the formulae.”

This was worked out in the following three chapters of this paper.

It ultimately leads then to the results that $\max P$ yields Maxwell’s exponential kinetic energy distribution as well as to the developments in Chapter V, which I will now discuss.

In Chapter V of this paper Boltzmann discusses the “Relation of the Entropy to that quantity, which I have called the [thermodynamic] probability distribution (9)”. He first makes the connection between what he calls the degree of permutability $\Omega$ or $\log P$ given by:

$$\Omega = -\int \int f(r, v)\log f(r, v)drdv$$

and the entropy. Here $f(r, v)$ is a continuous generalization of the discrete $w_j$ used before, giving the number of molecules at the position $r$ with velocity $v$. The maximum of $\Omega$ under the constraints that $N$ and $E$ are given, leads then again to the exponential Maxwell equilibrium velocity distribution. Noting that the degree of permutability $\Omega$ differs from the logarithm of
the permutability $P$ only by a constant, one has $\Omega = \log P + \text{constant}$. If the gas was initially not in thermal equilibrium and approaches equilibrium, $\Omega$ must reach a maximum $\Omega_{\text{max}}$. Boltzmann then computes thermodynamically the entropy $S$ for an ideal gas with $N$ particles and average kinetic energy or temperature $T$. For reversible processes he finds then:

$$S = \int dQ/T = \Omega = \log P + \text{constant}.$$  

As Abraham Pais remarks in his classic book “Subtle is the Lord...”[7]: “Boltzmann’s qualities as an outstanding lecturer are not reflected in his scientific papers, which are sometimes unduly long, occasionally obscure and often dense. Their main conclusions are sometimes tucked away among lengthy calculations.”

The paper I am discussing is a prime example of this description. Only in the text towards the end of the paper the following sentence appears referring to the previously obtained formula $S = \int dQ/T = \Omega$ when he says:

“Now it is known that when in a system of bodies only reversible changes occur, the total entropy of all these bodies remains constant. If, however, also irreversible processes occur, then the total entropy of the system must necessarily grow....”

According to the equation

$$d\Omega = d\log P = dQ/T = dS$$

the increase in the sum of the degree of permutability of a system $d\Omega$ equals then the increase of its entropy $dS$. He says:

“Therefore the degree of permutability $\Omega$ is a quantity, which in the equilibrium state, apart from a constant factor and an addend, is identical with the entropy $S$.”

That is: $S = c_1 \Omega + c'_2 = c_1 \log P + c_2$, but this formula is not in the paper.

Boltzmann ends this very long [60 pages] paper by remarking that too little is known both experimentally and theoretically about liquids and solids, to generalize his relation $S = c_1 \log P + c_2$ from ideal gases to liquids or solids. He remarks that he “has given earlier arguments that it is likely that also for these states of aggregation, thermal equilibrium will be determined by a maximum of the quantity $\Omega$, which [also] for such systems [would be] identical with the entropy $S$.”
III. Planck’s derivation of Boltzmann’s \( S = c_1 \log P + c_2 \) \[8\]

It was really Planck who made the step from Boltzmann’s paper to \( S = k \ln W + c \), where \( W \) is written instead of \( P \). Planck bases his discussion of the connection between entropy and probability on the universality of both the Second Law and the laws of probability, “so that it is to be expected that the connection between entropy and probability should be very close”.

Hence he makes the following proposition as the foundation of all further discussion: “The entropy of a physical system in a definite state depends solely on the [thermodynamic] probability \( W \equiv P \) of this state.”

Without knowing this probability \( W \), \( S \) can be determined as follows.

Planck’s derivation of Boltzmann’s \( S = f(W) \)

The probability \( W \), for a system consisting of two entirely independent systems with probabilities \( W_1 \) and \( W_2 \), respectively, is: \( W = W_1 W_2 \). Then \( S_1 = f(W_1) \) and \( S_2 = f(W_2) \). Second Law: \( S = S_1 + S_2 \) or \( f(W_1 W_2) = f(W) = f(W_1) + f(W_2) \). Differentiating both sides of this equation with respect to \( W_1 \) with \( W_2 = \text{constant} \) and then the resulting equation with respect to \( W_2 \) at \( W_1 = \text{constant} \) one obtains:

\[
\dot{f}(W) + W \ddot{f}(W) = 0
\]

with the solution: \( f(W) = k \log W + \text{constant} \) or \( S = k \log W + c \). Thus Planck formulated Boltzmann’s connection between entropy \( S \) and the permutability \( P \sim W \), in its definitive form:

\[
S = k \log W + c
\]

Planck notices two differences between his formula and Boltzmann’s \( S = c_1 \log P + c_2 \):

a) he replaces Boltzmann’s macroscopic expression for \( c_1 = R/N \) by a molecular quantity which he called Boltzmann’s constant \( k \).

b) the additive constant \( c_2 \) is undetermined as is the case in the whole of classical thermodynamics. Planck assigns a definite value to \( c_2 \), i.e. a definite value to \( S \), by using the “hypothesis of quanta”.

That is, he assumed that in every finite region of phase space the thermodynamic probability has a finite magnitude limited by [the existence of] \( h \), Planck’s constant, and can not be infinitesimally small like in the classical
case. This allows $S$ to be determined free of an arbitrary constant and at the same time to connect the classical and quantum mechanical values of $S$, such that $S = 0$ at $T = 0$ (Sackur-Tetrode formula)\cite{9}.

To the best of my knowledge neither Boltzmann’s nor Planck’s derivation of $S$ for an ideal gas has ever been generalized to an interacting gas. Results for such a gas can be obtained from Gibbs’ microcanonical ensemble but that is based ultimately on the unproven ergodic hypothesis.

IV. Einstein’s Objection\cite{10}

1. From 1905-1920 Einstein repeatedly objected to the probabilistic derivation of $S = k \log W + c$.
2. Basis: the thermodynamic probability $W$ to find the system in a certain complexion can only be determined dynamically and not be guessed statistically by assigning “ad hoc permutabilities” ($P$) to complexions of the system.
3. In fact, it is determined by the frequency that a phase space trajectory visits a given region of phase space due to its dynamics in phase space.

Quote of 1910\cite{10b}

“Usually $W$ equals the number of complexions. In order to compute $W$ [however] one needs a complete (molecular-mechanical) theory of the system. Therefore it is dubious that the Boltzmann principle has any meaning without a complete molecular-mechanical theory or some other theory which describes the elementary [dynamical] processes [of the system]. In equilibrium, the expression $S = k \log W + c$, seems [therefore] devoid of [any] content from a phenomenological point of view, without giving in addition such an elementary theory.”

V. The SRB distribution\cite{11}

Recently a theory has been developed for systems in a non-equilibrium stationary state, which are in principle, not restricted to be near equilibrium. This theory uses a probability or measure for “complexions”of the system in its phase space following Einstein’s dynamical rather than Boltzmann’s (probabilistic) Principle, as Einstein called it. This measure is usually called the Sinai-Ruelle-Bowen or SRB measure\cite{11}, which will be sketched in a physical way now. For simplicity, I will use a two dimensional representation.
Consider a smooth and very chaotic classical dynamical system (Anosov-like). This Chaoticity is based on the hyperbolicity of the points representing the system in its phase space. Each such point has two manifolds (cf.fig.1): a) an unstable manifold \((u)\), on which two separate points near a given phase point exponentially separate from each other; b) a stable manifold \((s)\) on which two separated points near a given phase point exponentially approach each other. The union of all unstable manifolds

![Figure 1: Unstable \((u)\) and stable \((s)\) manifolds associated with a phase point (thick bullet) in a two dimensional representation.](image)

of the phase points representing the system is called the \textbf{unstable manifold} in the system’s phase space; the union of all stable manifolds of the phase points representing the system is called the \textbf{stable manifold} in the system’s phase space. One now makes a \textbf{(Markov) partition} of the system’s phase space into “parallellograms” (cells) (cf.fig.2).

The “horizontal sides” of the parallelograms form together the unstable manifold and the “vertical” sides of the parallelograms form together the stable manifold in the phase space. The size of these parallelograms is determined by a parameter \(T\), so that for \(T \to 0\) their sizes go to zero. Now each cell \(E_j\) in phase space is given a weight \(\Lambda_{u,\tau}^{-1}(x_j)\) which is equal to the inverse of the phase space expansion along the unstable manifold, during a time \(\tau\). This phase space expansion is based on a trajectory moving during a (discrete) time \(\tau\) from \(-\tau/2 - 1\) to \(\tau/2\) along a phase space trajectory.
through the center $x_j$ of the cell $E_j$, using the dynamical equations of motion (cf.fig.3).

Considering a small phase space volume $A$ around the initial point at $-\tau/2 - 1$ (cf.fig.4), then all points in $A$ will go via phase space trajectories to corresponding points in the phase space volume $B$ around the final point at $+\tau/2$. The larger the phase space volume expansion $\Lambda_{u,\tau}(x_j)$ in the direction of the unstable manifold $u$ is, i.e. the larger $L_B/L_A$, the more the phase space trajectories will tend to avoid (bypass) the point $x_j$. The inverse of

Figure 2: Markov partition of a two dimensional phase space with cells $E_j$, formed by the unstable ($u$) and stable ($s$) manifolds of the phase points.

Figure 3: Trajectory segment of duration $\tau$ through the center $x_j$ of cell $E_j$ of a Markov partition of the system in phase space.
this ratio $\sim L_A/L_B \sim \Lambda^{-1}_{u,\tau}(x_j)$ will therefore be a measure of the “eagerness” or frequency of the phase space trajectories to be near $x_j$, i.e. that the system will visit the cell $E_j$. Weighing the Markov partitions in phase space this way, one obtains in a dynamical way the probability to find the system anywhere in phase space. As a consequence, the average of a smooth function $F(x)$, where $x$ denotes a point in phase space, is then determined by the SRB measure $\Lambda^{-1}_{\tau, u}(x_j)$:

$$\int \mu_{SRB}(dx)F(x) = \lim_{\tau \geq \tau/2 \to \infty} \frac{\sum_j \Lambda^{-1}_{u,\tau}(x_j)F(x_j)}{\sum_j \Lambda^{-1}_{u,\tau}(x_j)}$$

This appears to me a direct example of Einstein’s proposal of a probability for complexions based on the system’s dynamics rather than on ad hoc, although possibly reasonable, probabilistic assumptions as made by Boltzmann and Planck.

Figure 4: Small phase space volume of extension $L_A$ at time $-\tau/2 - 1$ and of extension $L_B$, in the direction of the unstable manifold $(u)$ at time $\tau/2$. $L_B/L_A$ gives the phase space volume increase in the direction of the unstable manifold $(u)$.

VI. Final Remarks

1. In thermal equilibrium the SRB distribution reduces to Gibbs’ micro-canonical ensemble. This implies that this ensemble can also be derived rigorously dynamically along the lines sketched here, albeit so far only for smooth and sufficiently chaotic systems. The role of coarse graining phase
space into physically infinitesimal cells, to go from a microscopic to a macro-
soscopic description, which is used in various ways in all classical derivations
of thermodynamics from statistical mechanics and also by Boltzmann and
Planck, is only used in passing in the SRB measure, because of the ultimate
\[ \lim_{T \geq \tau/2 \to -\infty} \]
2. To actually use Einstein’s dynamical method to determine the probabil-
ities of cells in phase space in practice, requires a solution of the equations
of motion. The only way, so far, around this fundamental difficulty has been
to replace the effects of dynamics again by suitable probability distributions
as is done e.g. in superstatistics\cite{12-14}. This has been applied successfully to
certain distribution functions in turbulent flows by using e.g. log-normal or
\[ \chi^2 \]-distributions.
3. To the best of my knowledge there is no definition of entropy beyond
the linear (near equilibrium) regime. This is in my opinion a fundamental
open question, whose solution may be essential to make real progress into the
far from equilibrium region. Gallavotti and I\cite{15} have conjectured that the
entropy in nonequilibrium stationary states “far” from equilibrium cannot be
defined, just like the heat content of a body in equilibrium cannot be defined,
since it depends on how this heat is used\cite{16}. Similarly, entropy differences
such as entropy production or entropy transfers could be meaningful also far
from equilibrium, just like heat production or heat transfer are in equilibrium.
4. In all fairness to Boltzmann, it should be said that he also proposed to
determine the probability of a state or a complexion of a system in a region of
phase space of this system in equilibrium, by assuming that this probability
would be proportional to the time the system spends in it i.e. involving the
dynamics of the system. But for some reason he did not develop this idea
further.

Finally it would be, in my opinion, a grave mistake to think that Boltz-
mann would have been opposed to these new dynamical developments. As I
said before, he had a strong disposition for dynamics and I think his prob-
abilistic work was presumably inspired to get rid of his many opponents to
his dynamical work and was just an intermezzo for him, important as it is
for us.

In fact, Boltzmann would have been delighted to see that a dynamical the-
ory of phase space weights was developed and used a century after his death
and that therefore his dynamical predilection was justified in the end\cite{17}. 
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