Is Irreversibility Intrinsic?

Einstein was convinced that thermodynamics was the only universal physical theory that will never be overthrown because he believed thermodynamics stands on general principles that are independent of the underlying details [339, p. 33]. However, a microscopic understanding of thermodynamics relies on the framework of the statistical mechanics of atoms and molecules. The term *irreversibility* was introduced into physics primarily in the context of the Second Law of Thermodynamics and determining whether the law was exact or an approximation became an overriding issue. In yet another letter from Maxwell to Tait, he explained that the point of his demon argument had been to demonstrate that the Second Law "has only a statistical certainty" [393] [394]. Ludwig Boltzmann (1844-1906) developed a statistical approach to explain the time-asymmetric and irreversible non-equilibrium behavior of macroscopic systems and insisted that such processes were determined by which states were the most probable to occur. Although Boltzmann's view eventually prevailed, the issue of entropy and irreversibility were highly contentious subjects in the second half of the 19th century, leading up to the discovery of the quantum [395] [396].

Einstein explained Brownian motion using Boltzmann's ideas and in Planck's discovery of the quantum, he was forced in desperation to accept Boltzmann's methods in order to explain the black-body radiation spectrum when nothing else would work. Objections to Boltzmann's ideas, in terms of the reversibility paradox in 1876 by Josef Loschmidt (1821-95) and by the recurrence paradox in 1896 by Ernst Zermelo (1871-1953), were part of the conflicts at the end of the 19th century over the roles of atoms and energy in scientific explanations of matter. In addition to these specific objections was the general but strenuous opposition by the *energeticists*, such as Wilhelm Ostwald, and Pierre Duhem, who tried to understand all physical processes merely with the help of concepts involving only pure energy, as well as by Ernst Mach who rejected atomic theory.

In a lecture at the 1944 centennial of Boltzmann's birth, the great mathematical physicist Arnold Sommerfeld (1868-1951), who made important contributions to the early formulations of quantum mechanics and whose students were Heisenberg and Pauli, described a debate at a meeting in Lübeck in 1895 between Ostwald, who denied the existence of atoms, and Boltzmann [357, p. 46] [397]:

See the print edition of The Quantum Measurement Problem for quotation.

This was an example of Planck's lament that "A scientific truth does not triumph by convincing its opponents and making them see the light, but rather because its opponents eventually die and a new generation grows up that is familiar with it." The opposition to Boltzmann by the older generation persisted despite the lack of new adherents.

However, Boltzmann's ideas were relevant to Maxwell's demon. Without a demon present, the gas of particles in Maxwell's box will eventually become uniformly distributed across both compartments *A* and *B*. This is irreversible in the sense that, in our experience, the particles do not find themselves all grouped in compartment A at a later time. Josef Loschmidt (1821-1895) objected that this irreversibility cannot be explained using only the laws of mechanics since these laws are reversible in time. Loschmidt demonstrated that any solution for the motion of the particles remains a solution when the velocities of all the particles are reversed at a particular time: $\bar{v}(t) \longrightarrow -\bar{v}(t)$, so that all processes will proceed in reverse. The particles could all very well end up in A at a later time if governed only by the reversible laws of mechanics. Some contemporary commentators would note with approval Boltzmann's supposed retort to Loschmidt: "Go ahead and reverse them!" However, Boltzmann's actual argument was that the distribution of particles depends not only on the laws of mechanics but also on the initial states of the particles. Loschmidt's theorem becomes a concern only for those initial states which lead to a very non-uniform distribution at a certain time but it doesn't prove that there are not more initial conditions that lead to a uniform distribution at the same time. Loschmidt's reversed swarm of particles was not impossible, just quite improbable [357, p. 98]. In fact, Boltzmann could demonstrate that there are vastly more uniform than non-uniform distributions so that there are a correspondingly much greater number of initial states which lead to them.

Niels Bohr had a strong interest in statistical mechanics beginning with his thesis work and with his 1913 quantum model of the atom. From Bohr's 1912 lecture notes is his hand-drawn sketch of an isolated mountain and a succinct description of what constitutes entropy that illustrates Boltzmann's argument in a very simple way: in terms of a man who finds himself wandering in a flat land, so that it may be said that in a year, it would also be expected to find him there, because it would be a strange coincidence if, on his way, he should just hit on the one sharply peaked mountain [398, p. 320].

Thirty years earlier, both Maxwell and Thomson (later Lord Kelvin) had also agreed with Bohr's view of Boltzmann's arguments in that they accepted an underlying reversibility for classical systems but they acknowledged that there are physical processes that were effectively irreversible. Maxwell gave an example of the consequences of listening only to Loschmidt [399]:

> Now *one thing in which the materialist (fortified with dynamical knowledge) believes is that if every motion great & small were accurately reversed, and the world left to itself again, everything would happen backwards: the fresh water would collect out of the sea and run up the rivers and finally fly up to the clouds in drops which would extract heat from the air and evaporate and afterwards in condensing would shoot out rays of light to the sun and so on. Of course, all living things would regrede from the grave to the cradle and we should have a memory of the future but not of the past.*
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> The Scientific Letters and Papers of James Clerk Maxwell, Volume II, P.M. Harman (Ed), Cambridge University Press, Reissue Edition, 1995.

Boltzmann also responded to Loschmidt by working out his statistical interpretation of the Second Law in detail, which appeared in his 1877 paper, "On the relation between the second law of the mechanical theory of heat and the probability calculus with respect to the theorems on thermal equilibrium." For each microscopic state of a macroscopic system, Boltzmann allocates an entropy, S_B, which accurately characterizes isolated systems and increases to describe the approach to equilibrium where its value then agrees with Clausius' entropy *S*. Boltzmann associates each macroscopic state *M* with an entropy that also represents every microscopic state *m* in the phase-space volume Γ_M associated with *M*:

$$S_B\big(M(m)\big) \propto \log \Gamma_{M(m)}.$$

Max Planck introduced the notation for the entropy that now appears on Boltzmann's tombstone:

$$S_B = k \log W,$$

where *k* is Boltzmann's constant and W is the number of microstates by which the macroscopic state *M* can be realized. For non-equilibrium systems, this identifies the increase in entropy with increases in the volume of the occupied phase space region. Macroscopic systems have a very large number of degrees of freedom and Boltzmann's approach captures the *typicality* of the actually observed irreversible behavior. Rare events, such as the spontaneous separation of gas particles into side A, would occur only over times longer than the age of the universe. This feature of Boltzmann's statistical theory also answered Zermelo's objection based on Henri Poincaré's (1854-1912) *recurrence theorem*. Poincaré had shown that any bounded system will almost certainly return to a state that is arbitrarily close to its initial state. However, Boltzmann easily showed that the recurrence times for any macroscopic system would be so enormous as to be irrelevant.

Boltzmann's approach brought probability into science at a time when determinism was dominant. The entropy can be expected to increase with time if the system has been initially prepared in a low-entropy state, which can be easily arranged by [400]

> *"experimentalists who are themselves in low-entropy states…born in such states and maintained there by eating low-entropy foods, which in turn are produced by plants using low-entropy radiation coming from the Sun, and so on."*

This line of reasoning leads unavoidably to the question of the initial state of the universe having a very small Boltzmann entropy. Richard Feynman notes that understanding irreversibility requires adding to the physical laws the hypothesis that in the past the universe was more ordered than it is today [401]. Roger Penrose argues that the initial state just after the Big Bang has an approximately uniform energy density with low entropy [402, p. 702].

Boltzmann generalized Maxwell's approach for the kinetic theory of gases to non-equilibrium processes, deriving what is now called the *Boltzmann equation*, describing the approach from non-equilibrium to equilibrium in terms of collisions of the particles. Based on this, he attempted a derivation of irreversibility in thermodynamics based on the underlying classical mechanics of colliding particles that he considered equivalent to the law of entropy increase. This was formulated in terms of a function H identified with negative entropy for which

$$\frac{dH}{dt} \leq 0$$

where the equality holds if and only if thermal equilibrium is reached. This is Boltzmann's *H-theorem*. Since classical mechanics is reversible in time, Boltzmann had to have made an assumption in his derivation that breaks time symmetry but identifying it precisely turned out to be subtle. It was finally found during a debate in the pages of Nature during the 1890s [396]. The assumption (later called the assumption of *molecular chaos* or *Stosszahlensatz*) was that the velocities of colliding particles are uncorrelated and independent of position. Therefore, an assumption of disorder had been made. The status of Boltzmann's molecular chaos assumption was later reconstructed by Paul and Tatiana Ehrenfest in 1912 [403], which led to renewed interest in the related but difficult concept of the ergodic theorem equating statistical averages and time averages [395]. Observations of physical quantities during experiments last a finite duration which may be extremely long on the microscopic level, allowing the microstate to experience many collisions, so that time averages are empirically significant. The ergodic theorem was revisited and clarified by von Neumann and Birkhoff in the 1930s after the development of quantum statistical mechanics.