

PLANCK'S STATISTICAL HERITAGE:
BOLTZMANN ON IRREVERSIBILITY

Electromagnetic radiation in a perfectly absorbing cavity is not the only physical system that moves irreversibly to equilibrium. If, for example, the velocity distribution of the molecules of a gas is initially different from Maxwell's, intermolecular collisions will produce that distribution with the passage of time and will thereafter maintain it. At least, that should be the case if the Maxwell distribution is, as its author claimed, the only one that remains stable as molecules continue to collide within the gas. Concern like Planck's with the second law of thermodynamics was not, therefore, the only motive for considering irreversibility. The natural way to show the uniqueness of the Maxwell distribution is to demonstrate that an arbitrary initial distribution of molecular velocities must, over time, evolve into and stabilize at Maxwell's form. Planck's electromagnetic problem, though not initially his motives, had had a precise parallel in gas theory.¹

Until the end of the nineteenth century, however, only Boltzmann devoted significant attention to a kinetic theory of irreversibility. His first formulation appeared in 1872,² early in his career, and he repeatedly returned to the subject throughout his professional life, partly to generalize and extend his first result and partly to defend it against often cogent criticism. Those criticisms and Boltzmann's response to them are the sources of three interrelated sets of ideas which were to re-emerge in Planck's research as he approached the version of black-body theory that ultimately transformed physics.³ The first set clusters about Boltzmann's so-called *H*-theorem, an apparent proof from mechanics that a gas must evolve to equilibrium from an arbitrarily chosen initial state. That proof and Boltzmann's initial interpretation of it are the subjects of the two sections that follow. The third section is devoted to a second set of ideas, derived from the very different probabilistic or combinatorial treatment of irreversibility which Boltzmann developed during 1877 to defend the *H*-theorem against

paradox, but which also altered his understanding of what that theorem proved. Even with those alterations the H -theorem was not free from difficulties, and Boltzmann's wrestling with them produced a third conceptual cluster centering on the notion of "molecular disorder," to be discussed in the fourth and fifth sections below. Planck's simultaneous resort to the first and third of these sets of ideas will be treated in Chapter III. His first use of the second is a central theme of Chapter IV.

Boltzmann's H -theorem

Boltzmann's proof of irreversibility, the H -theorem, appeared in several versions, and Planck probably first encountered the somewhat simplified form developed for the opening chapter of Boltzmann's *Lectures on Gas Theory*, of which the first volume was published in 1896.⁴ For present purposes, the accompanying discussion, which includes Boltzmann's only developed presentation of his recently conceived notion of molecular disorder, is more important than the proof itself. But unfortunately the discussion is incomprehensible without a prior knowledge both of the structure of Boltzmann's demonstration and of the debates it had previously provoked.

After a brief introduction, "A Mechanical Analogy for the Behavior of Gases," Boltzmann opens the first chapter of the *Gas Theory* by asking his readers to consider a container filled with a gas consisting of identical, perfectly elastic spherical molecules. Then he introduces a function f of velocity and time such that $f(u, v, w, t) du dv dw$ (usually abbreviated thereafter as $f d\omega$) is the number of molecules per unit volume that, at time t , have velocity components between the limits u and $u + du$, v and $v + dv$, and w and $w + dw$.⁵ That function, $f(u, v, w, t)$, specifies the velocity distribution of molecules in the container at each instant of time. For simplicity, Boltzmann next introduces two additional assumptions which he later shows how to eliminate: the molecules are exposed to no external forces, and the walls of the container are perfectly smooth and elastic. On these assumptions, he writes:

the gas is exposed to the same conditions everywhere within the container. It follows that, if at the beginning of some time interval the number of molecules per unit volume with velocity components between the [above] limits is on the average the same at each position in the gas . . . , the same will hold at all future times.⁶

Elsewhere Boltzmann mentions a further condition, also required by

the argument he is about to develop. His derivation requires the assumption that the volume $d\omega$ "is infinitesimal, but still contains a very large number of molecules."⁷

For simplicity, Boltzmann takes his molecules to be perfectly elastic spheres of diameter σ , and he then examines a collision between two of them, one initially contained in the velocity cell $d\omega$, the other in $d\omega_1$. To specify the collision further, he also posits that the line connecting the centers of the two molecules at the instant of collision lies in an infinitesimal cone of solid angle $d\lambda$ and given axial direction. All collisions between molecules originating in $d\omega$ and $d\omega_1$ and for which the line of centers is contained in $d\lambda$ will, Boltzmann writes, "for the sake of brevity be called 'collisions of the specified kind'."⁸

Boltzmann's next problem is to evaluate the number dv of such collisions occurring in a unit volume during a time interval dt . For that purpose he elaborates a now standard technique first developed by Clausius to investigate the mean free path of gas molecules. Imagine a moving sphere of radius σ (twice the radius of an individual molecule) moving with velocity g , equal to the relative velocity of two molecules contained in $d\omega$ and $d\omega_1$, respectively. Any collision of the specified kind is equivalent to an encounter between the sphere and a fixed point provided that the fixed point lies in the surface element intercepted by the cone $d\lambda$ on the sphere. As the sphere moves during time dt , that surface element sweeps out a cylinder of volume $\sigma^2 d\lambda g \cos \theta dt$, where θ is the angle between the direction of the sphere's motion and the axis of the cone ($-\pi/2 < \theta < \pi/2$). If the sphere represents a molecule initially in $d\omega$, then the density of the points with which it can make a collision of the specified kind is $f_1 d\omega$, and the total number of such collisions during dt will be $f_1 d\omega_1 \sigma^2 d\lambda g \cos \theta dt$. (Here, f_1 is an abbreviation for $f(u_1, v_1, w_1, t)$; similar abbreviations will enter below without special comment.) Since, in addition, molecules in $d\omega$ have a density $f d\omega$, and since any one of them may enter into a collision of the specified kind, the total number of such collisions occurring in a unit volume during dt is given by⁹

$$dv = f d\omega f_1 d\omega_1 \sigma^2 d\lambda g \cos \theta dt. \quad (1)$$

Treating the same problem today, a physicist would describe that equation as yielding the average number of collisions. But Boltzmann, though he surely knew the difference, does not explicitly distinguish the average from the actual number of collisions, a fact that will shortly be important.

Having analyzed the rate at which collisions occur, Boltzmann calls upon the laws of mechanics to determine the velocity cells, $d\omega'$ and $d\omega'_1$, in which molecules initially in $d\omega$ and $d\omega_1$ will be found after a collision. These new cells, he shows, have two important properties. First, $d\omega' d\omega'_1 = d\omega d\omega_1$. Second, a collision between molecules initially in the new cells $d\omega'$, $d\omega'_1$ will just return those molecules to the original cells $d\omega$, $d\omega_1$. Boltzmann contrasts these collisions, which he calls "collisions of the inverse kind,"¹⁰ with the ones that originated in $d\omega$, $d\omega_1$. The latter, his collisions of the specified kind, remove molecules from $d\omega$ and $d\omega_1$, thus reducing the values of f and f_1 . Inverse collisions, on the other hand, return molecules to $d\omega$ and $d\omega_1$, thus increasing the corresponding values of the distribution function. Both sorts of collisions are going on in the gas at all times, and the rates at which molecules enter and leave $d\omega$ and $d\omega_1$ can therefore readily be computed from equation (1). By combining previously derived results, Boltzmann can provide a formula for the rate at which the distribution function itself changes. It proves to be¹¹

$$\frac{\partial f}{\partial t} = \iint (f'f'_1 - ff_1)\sigma^2 g \cos \theta d\omega_1 d\lambda. \quad (2)$$

The preceding formula is a special case of the so-called Boltzmann equation, perhaps its author's most important contribution to science (its centenary was celebrated by a special meeting in Vienna in 1972). But it entered physics, not for its own sake, but simply as an intermediate step on the way to the H -theorem, and Boltzmann scarcely paused in his argument before putting it to work. Immediately after presenting equation (2) in the fourth numbered section of the first chapter of the *Gas Theory*, Boltzmann proceeds to its application in a new section called "Proof that the Maxwell Velocity Distribution Is the Only Possible One."¹² Its argument is mathematically complex but conceptually straightforward, so that only its result is required here. Boltzmann first defines a function $H(t)$ by the equation^{13†}

$$H(t) = \int f \log f d\omega. \quad (3)$$

Then he shows that

$$\frac{dH}{dt} = -\frac{1}{4} \iiint [\log(f'f'_1) - \log(ff_1)][f'f'_1 - ff_1]\sigma^2 g \cos \theta d\omega d\omega_1 d\lambda. \quad (4)$$

In the integrand of that equation, the two expressions in brackets are

either both positive, both negative or both zero, so that $dH/dt \leq 0$. The equality sign, furthermore, obtains only if $f'f'_1 = ff_1$, a condition from which the Maxwell distribution can easily be shown to follow. Those results constitute Boltzmann's H -theorem. The function H , defined by equation (3) for an arbitrary initial distribution, can only decline to a minimum with the passage of time. As it reaches its minimum value, the distribution becomes Maxwell's, and that distribution is thereafter maintained. "We have shown," Boltzmann said, "that the quantity we have called H can only decrease, so that the velocity distribution must necessarily approach Maxwell's more and more closely."¹⁴

After an intervening section, "The Mathematical Meaning of the Quantity H " (to be considered in a later part of this chapter), Boltzmann puts the H -theorem to work. First he shows, by already standard techniques, that when $dH/dt = 0$ and the Maxwell distribution obtains, then Boyle's, Charles's, and Avogadro's laws all follow if temperature is equated with the mean translational energy of a molecule. Next, by equating heat content Q with total kinetic energy, Boltzmann derives an expression for the specific heat of a gas. Finally, he returns to the function H , now evaluated for the whole of a gas in a container rather than for a unit volume, and he proves by a lengthy but presently irrelevant argument a consequential theorem about it. When H has reached its minimum or equilibrium value, $H_{\min}$, it can differ from the negative of the entropy of the gas only by an arbitrary additive constant. Boltzmann shows, in short, that

$$\Delta H_{\min} = -\frac{\Delta Q}{T} = -\Delta S, \quad (5)$$

where the variation Δ is taken along a reversible path, the gas being maintained in equilibrium. At least for reversible processes, Boltzmann has derived the second law by combining mechanical and statistical premises.¹⁵

The first interpretation of the H -theorem

The preceding sketch of the H -theorem and its immediate consequences is modeled on Boltzmann's presentation in the first chapter of the *Gas Theory*, because Planck, who cites no other sources in which the theorem occurs, presumably found it there.^{16†} But the parts of the *Gas Theory* so far selected for discussion differ only in mathematical detail from the corresponding portions of Boltzmann's original presen-