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On the Mechanical Explanation of Irreversible Processes *

ERNST ZERMELO

SUMMARY

Boltzmann has conceded [Selection 8] that the commonly accepted version of the second law of thermodynamics is incompatible with the mechanical viewpoint. Whereas the author holds that the former, a principle that summarizes an abundance of established experimental facts, is more reliable than a mathematical theorem based on unverifiable hypotheses, Boltzmann wishes to preserve the mechanical viewpoint by changing the second law into a "mere probability theorem", which need not always be valid.

Boltzmann's assertion, that the statistical formulation of the second law is really equivalent to the usual one, is based on postulated properties of the *H*-curve which he has not proved, and which seem to be impossible. His argument that any arbitrarily chosen initial state will probably be a maximum on the *H*-curve, if it were valid, would prove that the *H*-curve consists entirely of maxima, which is nonsense.

The only way that the mechanical theory can lead to irreversibility is by the introduction of a new physical assumption, to the effect that the initial state always corresponds to a point at or just past the maximum on the *H*-curve; but this would be assuming what was supposed to be proved.

My paper in the March issue of this Journal, "On a theorem of dynamics and the mechanical theory of heat,"† has drawn from Herr Boltzmann an immediate reply,‡ in which I find a confirma-

* [Originally published under the title: "Ueber mechanische Erklärungen irreversibler Vorgänge", *Annalen der Physik* 59, 793–801 (1896).]

† E. Zermelo, *Ann. Physics* 57, 485 (1896). [Selection 7]

‡ L. Boltzmann, *Ann. Physik* 57, 773 (1896). [Selection 8]

tion of my own views rather than a contradiction. Not only does Herr Boltzmann recognize that the basic theorem of Poincaré is "obviously correct", but he also concedes that it is applicable to a closed system of gas molecules in the sense of the kinetic theory. Indeed, in such a system all processes are *periodic* from a mathematical viewpoint, hence *not irreversible* in the strict sense, so that one may not assert that there is an actual progressive increase of entropy as the second law, in its usual meaning, would require. To prove this, and thereby to obtain a firm basis for the discussion of the principal questions, was the purpose of my paper; at the time I was not familiar with Herr Boltzmann's investigations of gas theory, but I still think that this general clarification was not at all superfluous.

The "necessity of making a fundamental modification either in the Carnot-Clausius principle or the mechanical viewpoint" which I asserted is therefore conceded, and it remains a matter of personal opinion which of these possibilities is to be chosen. As for me (and I am not alone in this opinion), I believe that a single principle summarizing an abundance of established experimental facts is more reliable than a mathematical theorem, which by its nature represents only a theory which can never be directly verified; I prefer to give up the theorem rather than the principle, if the two are inconsistent.

Herr Boltzmann, however, will not modify the ordinary mechanical viewpoint, and instead wishes to change the second law into a "mere probability theorem" which is not valid at all times. Yet he asserts that this change, whose *principal* meaning he does not misunderstand, is really unimportant, and that "in practice" his two formulations are "completely equivalent". Let us see how far he has succeeded in proving this.

It is undoubtedly correct, as Boltzmann emphasizes, that for a very large number of molecules in a finite volume the average duration of the Poincaré period, the time after which a state will recur, is much too large for us to expect to make a direct *observation* of the theoretical periodicity. However, his numerical estimate, which is based on a single exceptional initial state with a

completely determined molecular configuration, is not conclusive. In practice one is interested in a "physical state" which can be realized by many possible combinations, and can therefore recur very much earlier. Moreover, for my purposes it is sufficient to prove the recurrence of any other state with the same or a smaller value of the entropy; the periods of recurrence of such individual values of the entropy S will of course vary, but on the whole they no longer come out to be so "comfortingly" large. Nevertheless there are functions whose periodicity is beyond observation, and the entropy function might be one of them.

For such a function it can of course happen that it *appears* to be continually increasing, since the decreasing branch of the curve, which is theoretically always present, begins so much later that it does not need to be considered. Yet it by no means follows from this that there are functions for which one *always* observes the increasing and not the decreasing part, which is the property that the mechanical analog of the entropy function must have. It is not satisfactory simply to accept this property as a fact for a particular type of initial state that we can observe at present, for it is not a question of a variable which is just observed once (as for example the eccentricity of the earth's orbit) but of the entropy of *any arbitrary* system free of external influences. How does it happen, then, that in such a system there always occurs only an *increase* of entropy and *equalization* of temperature and concentration differences, but never the reverse? And what right do we have to expect this behaviour to continue, at least for the immediate future? A satisfactory answer to this question must be given, if we are to accept a mechanical analog of the second law.

It seems to me that probability theory cannot help here, since every increase corresponds to a later decrease, and both must be equally probable or at least have probabilities of the same order of magnitude. My opinion, in agreement with Poincaré's definition,† is that the probability of occurrence of a certain property of the molecular states, for example for a definite value of the function S ,

† H. Poincaré, *Acta Math.* 13, 71 (1890). [Selection 5, p. 199]

can be measured only by the "extension"† γ of the "region" g of all possible states which have this property, divided of course by the total extension Γ of the region G containing all possible states. But since according to Liouville's theorem each extension γ is independent of time, any such value of a function must have the same probability at a later time as at the initial time, and no overall increase or decrease is to be expected on the grounds of probability theory.‡

Herr Boltzmann proceeds in a different way. He assumes a function H whose curve, drawn with the time t as abscissa, runs in general very close to the t -axis but occasionally has elevations or "peaks". The larger the peaks are, the more improbable they are, and the less often they occur.§ I cannot find that he has actually *proved* this property from his other definition of the H -function. According to my definition, probability and duration of a state are not identical. Nevertheless, functions of the indicated nature may exist. He further assumes that the H -function has initially an unusually large value H_0 , corresponding to a peak, but soon passes this peak and decreases almost to zero. Finally, it runs very close to the abscissa axis for a very long time. This limiting value zero of the H -function corresponds to a velocity distribution expressed by Maxwell's law, so that the properties of this H -curve provide an explanation of the probability-theoretic meaning of the distribution law, which however I do not dispute. The law does not represent a "stationary *final* state" in the strict sense, since the curve eventually rises to new peaks after a long time. Herr Boltzmann himself considers the Maxwellian state to be the "*final* state" only in an empirical or approximate sense, and it seems to me that *this* assertion does not follow sufficiently clearly from his earlier writings.

† E. Zermelo, *Ann. Physik* 57, 485 (1896). [Selection 7, p. 210]

‡ [This argument is developed in more detail by Gibbs in his discussion of the generalized H -theorem: see *Elementary Principles in Statistical Mechanics* (Scribner, New York, 1902) Chapter XII.]

§ L. Boltzmann, *Ann. Physik* 57, 773 (1896). [Selection 8, p. 220]

But it is not here a question of Maxwell's law, but of whether an analogy exists between the properties of the H -curve and the second law of thermodynamics; it is this analogy that I dispute. It is not sufficient to show that all perturbations *finally* relax to a long-lasting equilibrium state; rather it is necessary to show that changes always take place in the same sense, in the direction of equalization; that the H -function *always only* decreases during observable times, or at least that there can only be very small, practically unnoticeable increases, which will always be immediately washed out by stronger decreases. In my opinion this proof is as little possible for the H -function as for any other function. Clearly the initial state, whose probability can depend only on the initial value H_0 , can just as well lie on a rising as a falling branch of the curve, and in the former case there must first be an *increase*, which can last just as long as the subsequent decrease. For this period we have $H > H_0$. Each observed decrease $H_1 \dots H_2$ in the falling branch corresponds to an equally great increase $H_2 \dots H_1$ in the rising branch, and the process is no more likely to begin in one way than the other. If the increase takes place in a shorter time and is hence less probable than the decrease—an assumption for which there is no basis in the theory—then it would still have to be *steeper* and therefore should be given just as much weight.

Herr Boltzmann's assertion, if I have understood it correctly,† is that the initial state has a fairly large H -value, say $H_0 > H'$, on a peak which is not too large (so that it does not have too small a probability) and as a rule must represent a *maximum*, so that of course one always observes only the decreasing branch. I cannot conceive of such a curve. Suppose for the sake of argument that the intersections of the H -curve with a line parallel to the time-axis at a height $H = H_0$ are mostly maxima, and that $H_0 > H'$. But where are the other points on the peak ($H > H'$) which are *not* maxima? Are they in fact in the minority compared to the

† L. Boltzmann, *Vorlesungen über Gastheorie* 1, 44 (1896) [p. 59 in the English translation].

maxima? It is clear that this argument can make sense only if the maxima are considered not as mathematical points but as having a certain breadth, i.e. a certain time-duration. But then for any initial state the value of the function will remain constant for a longer or shorter time, thereby representing a sort of labile equilibrium; whereas according to experience, for example in the case of heat conduction, the process of equalization begins more rapidly, the greater the initial temperature differences are, that is, the further the initial state is from the stable equilibrium state.

Aside from this, I do not understand what the *initial* state has to do with the argument, except for its property of having a small probability, which it shares with the neighbouring states. Herr Boltzmann assumes that the entire *H*-curve, and therefore the collection of all states through which the system passes, is *given* and now asks for the probability of a certain initial state, i.e. the place on the curve where the system actually begins to move, without any external forces being present. But, as experience teaches, there is no procedure available for producing *any arbitrary* initial state by an appropriate action and then isolating the system and letting it run by itself; one cannot make any arbitrary state P_0 the initial state. If this were true, then the system would actually pass through all the states P that follow P_0 in the series, while the previous states could only be added mathematically. Now if the above argument were correct, and the initial state represents a maximum of the *H*-function in most cases, then the same must also be true of *all other* states for which *H* exceeds H' , since any other state could be chosen as initial state. Moreover, the whole probability argument is just as applicable to any arbitrary state as to the initial state. All these states must therefore represent maxima, and the curve must consist purely of maxima above a certain height. This is nonsense, since the function cannot be constant. Therefore in order to obtain an approximate empirical analog of the entropy theorem, it is not sufficient to assume that the initial state is extraordinarily improbable; rather one must add the *new assumption*, that at the beginning the *H*-curve has a maximum or has just passed a

maximum. But as long as one cannot make comprehensible the *physical origin* of the initial state, one must merely assume what one wants to prove; instead of an explanation one has a renunciation of any explanation.

I have therefore not been able to convince myself that Herr Boltzmann's probability arguments, on which "the clear comprehension of the gas-theoretic theorem"† is supposed to rest, are in fact able to dispel the doubts of a mechanical explanation of irreversible processes based on Poincaré's theorem, even if one renounces the strict irreversibility in favour of a merely empirical one. Indeed it is clear *a priori* that the probability concept has nothing to do with time and therefore cannot be used to deduce any conclusions about the *direction* of irreversible processes. On the contrary, any such deduction would be equally valid if one interchanged the initial and final states and considered the *reversed* process running in the opposite direction. Hence, the following dice game is more relevant than the example introduced by Herr Boltzmann. Two dice-players, let us suppose, have made the observation that dice they obtain from a certain source always behave in a certain way when they first start to play with them. One particular face, say the one, always comes up first. In the first 600 throws, the one comes up 200 times rather than 100 times. However, in the next 6000 throws the ones are less frequent, and after the game has continued a long time they find that one comes up on the average only 100 times out of 6000, like all the other numbers. The first player sees nothing strange in this behaviour, since the laws of probability theory are supposed to apply to very long games. But the second player says: No! This dice must be false, and it is only through long use that it gradually regains its proper condition—the latter interpretation corresponds to my own opinion.

Not only is it impossible to explain the general *principle* of irreversibility, it is also impossible to explain individual irreversible

† L. Boltzmann, *Ann. Physik* 57, 773 (1896). [Selection 9, p. 226]

processes themselves without introducing new physical assumptions, at least as far as the time-direction is concerned. In particular, the differential equation for heat conduction and diffusion is

$$\frac{\partial u}{\partial t} = a^2 \frac{\partial^2 u}{\partial x^2}$$

and this equation can only represent irreversible processes. The attempt to derive this equation purely from the basic equations of mechanics, together with probability assumptions, which has been made for example by Clausius, Maxwell, and Boltzmann, cannot reach its goal, since it is an impossible undertaking, and an apparent success can only rest on an error of deduction. The major fallacy in the methods heretofore applied seems to me to be the unprovable (because untrue) assumption that the molecular state of a gas is always, in Boltzmann's expression, "disordered" and that all possible directions and combinations are equivalent, if one can say nothing definite about the true state, which must nevertheless depend on the "ordered" initial state.† Probability theory justifies such assumptions to a certain extent for the *initial state*, at most; the probability of a later state, however, and therefore the process itself, must always first be expressed in terms of the corresponding initial state, and only then can one decide on the permissibility of such averaging assumptions. The difficulty of carrying out investigations *rigorously* from the viewpoint of probability theory may be very great, but they do not seem to me to be insurmountable. In any case such investigations cannot by themselves correct the errors of the "statistical method" used up to now; questions of principle, such as those under discussion here, require arguments whose mathematical validity is beyond question. For the present I must restrict myself to these remarks; I hope later to return to a more explicit treatment of these methodological questions.

The great successes of the kinetic theory of gases in the explanation of *equilibrium* properties do not entail its applicability to

† Boltzmann, *Gastheorie* 1, 21 (1896) [p. 40 in the English translation].

time-dependent processes also, for the two are separate subjects; while in the former case the theory frequently gives us a correct and valuable picture, in the latter case, especially where it is a question of the explanation of irreversible processes, it must necessarily fail unless completely new assumptions are added to it.

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