Zermelo, Boltzmann, and the recurrence paradox

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(Received 5 October 1981; accepted for publication 10 December 1982)

The papers exchanged by Ludwig Boltzmann and Ernst Zermelo concerning the recurrence paradox are summarized. The historical context of the paradox, Zermelo's proof of the paradox, his opinions of its consequences, Boltzmann's reply, and the ensuing discussion are described.

INTRODUCTION

In late 1896 and 1897 Ernst Zermelo and Ludwig Boltzmann debated whether statistical mechanics could adequately explain the laws of thermodynamics. The four articles which make up the debate are, in spite of their age, of more than historical interest; the ideas are surprisingly current. Indeed the 85-year-old debate is still discussed and still without a clear-cut victor.

The articles are part of the attempt to use statistical mechanics to explain natural phenomena. Historically the growth of the essentially descriptive gas laws and laws of thermodynamics was followed by explanations of these phenomena by applying statistics to the hard-sphere model of a gas.

For example, A. Krönig in 1856, successfully related macroscopic quantity of pressure with the microscopic bouncing of gas of hard spheres off the walls of a container.[1] He derived a single-valued function which related the mass and velocity of the gas molecules to the pressure. (For further reading, the work of Paul and Titiana Ehrenfest[2] is an excellent review of the history of statistical mechanics.)

At roughly the same time that Krönig published his thesis in statistical mechanics, thermodynamics solidified another concept. In 1857, with the work of Sadi Carnot and Lord Kelvin as a base, Rudolf Clausius[3] published his finding that the ratio of the heat content of a system to its absolute temperature would always remain constant or increase. Eventually Clausius named this concept entropy. Kelvin called it the degredation of energy; the law of disorder is another descriptive name. In essence the second law describes nature as tending toward the disorder of matter and the dilution of energy. The task of statistical mechanics is now to explain this law of disorder.

Ludwig Boltzmann rose to the task. By 1872 he and James Clerk Maxwell had developed the distribution function which bears their names. The function relates the number of molecules in a given energy state to the energy of the molecules. It has the form

$$f\Delta\tau = \alpha e^{-\beta\epsilon}\Delta\tau ,$$

where $\Delta\tau$ defines the small range of speeds, α and β are constants, and ϵ is the total energy.

Armed with this distribution function Boltzmann set out to find a single-valued function of the coordinates of the system which acted like entropy.

The result was the H function[4]:

$$H = \Sigma f \log f \Delta\tau .$$

Calculation of the H function leads to a constant decrease in value with increasing time. The value of H acts exactly the reverse of entropy, entropy constantly rising and the H value constantly lowering. Boltzmann had apparently succeeded in finding a single-valued function of the coordinates which acted like entropy.

Not everyone, however, was convinced that Boltzmann was correct or indeed that their could be any single-valued function of the coordinates of the hard spheres which acted like entropy. Loscmidt pointed out in 1876 that Newton's Laws are symmetrical with time reversal while Boltzmann's function is not.[5] This is called the reversing paradox (Umkehr Einsatz). In 1896 Zermelo published the article which began the exchange which is the subject of this paper.

Boltzmann made some changes in his H theorem but this did not quiet the detractors–Zermelo[6] in 1900, Henri Poincaré[7] in 1906 among others. Indeed Boltzmann has not succeeded to this day, as Ilya Prigogne points out in *From Being To Becoming*,[8] mentioning Boltzmann's H theorem and Zermelo's recurrence in the same paragraph.

Though few admit it, the argument involves more than just using statistics to help Newton's laws explain Clausius's equation. The change in entropy depends on the direction of time; if time were reversed, so would the sign in the change in entropy. Thus explaining the change in entropy is closely related to explaining the direction of time which in turn impinges on what one feels is the nature of the universe. Would God order His universe through chance occurrences? The discussion becomes tinged with emotion.

In reading the papers one can sense Boltzmann's impatience with the refusal of some of the scientific community to accept his ideas. In 1906 Boltzmann committed suicide after fits of mental depression, aggravated, it was said, by the opposition to his views.

There is further reason to resurrect four 85-year-old papers. Both Zermelo and Boltzmann were great intellects. Their sharp interchange helps to further ones own understanding of statistical mechanics.

CONCERNING A LAW OF DYNAMICS AND THE MECHANICAL THEORY OF HEAT

Zermelo's first paper[9] in the series was published in 1896. He announced in the first paragraph "...in a system of point masses...a particular arrangement of masses, once assumed, must recur." When an arrangement of point masses recurs, so must any single-valued function of their coordinates. Entropy "continually" increases, a function of point-masses cycles. Thus a function of point masses cannot explain entropy.

As Zermelo said "...either the Carnot–Clausius principle or the statistical mechanical view of nature must be reformulated, if one cannot give up the latter entirely."

Zermelo had used a theorem of Poincaré[10] to prove that any system of mass points must cycle. Zermelo offers his readers his own version of the proof of that theorem. He uses what has become known as the continuity of phase space. The notation is Zermelo's.

A system of N point masses has $n = 6N$ variables, $3N$ coordinates and $3N$ velocity components. Differentiating with respect to time, the first $3N$ are the velocity components and the second $3N$ the acceleration components, that is, the force. The velocities are independent of the position and the accelerations are independent of the velocities. The equations have the form

$$\frac{dx_\mu}{dt} = X_\mu(x_1,x_2,...,x_n)\,. \qquad (1)$$

None of the variables X_n contain the variable x_n so that

$$\frac{\partial X_1}{\partial x_1} + \frac{\partial X_2}{\partial x_2} + \cdots + \frac{\partial X_n}{\partial x_n} = 0\,. \qquad (2)$$

[This condition is necessary for Eq. (1) to be an analytic function and Liouville's theorem to be valid.]

In such a system the initial state

$$x_1 = \xi_1\,, \quad x_2 = \xi_2 ... x_n = \xi_n \quad (t = t_0)$$

corresponds to a definite changed state expressed through the integral of Eq. (1):

$$x_\mu = \phi(t - t_0; \xi_1, \xi_2, ..., \xi_n)\,. \qquad (3)$$

A group of initial states g_0 corresponds to a definite later group g_t. He defined as the "area" of g_0 the n times integral

$$\gamma_0 = \int d\xi_1\, d\xi_2 ... d\xi_n\,,$$

which corresponds to the group of initial states. For any other state there is another area:

$$\gamma = \int dx_1\, dx_2 ... dx_n\,.$$

Since the function satisfies Eq. (2), Liouville's theorem is valid and the second integral equals the first and

$$d\gamma = dx_1 dx_2 \cdots dx_n = d\gamma_0 = \text{const}\,. \qquad (4)$$

Thus the succeeding states will have equal areas.

Zermelo defines a group of states, G_0, as the "future" of g_0 by demanding that G_0 contain all the states which follow the initial state. Each new state also has a future, G. Since all future states which follow g_0 were in the earliest G, G can only decrease. New states can never enter. Equation (4) is still valid, however, and so the area of G too, must remain constant. A state leaving G, Zermelo says, cannot be of finite area and he names these states "singular."

"Now g_0 is contained in G_0 and must be part of an overwhelming number of latter futures G_t." This in turn means that there are states in the future which must return to g_0; g_0 must recur. "It follows directly," Zermelo continues, "that there can be no single valued continuous function of the coordinates of the states, $S(x_1,x_2,...,x_n)$ which continuously increases." Each time a state returns so must the value of S.

There is a simple proof of this. If the function S continuously increases for all initial states of g, then it must do the same for all states of the larger group G, the future of g. Because of Eq. (4), the integral over G,

$$\int S\, dx_1\, dx_2 \cdots dx_n\,,$$

must continuously increase. This is impossible...since G does not change. The value of the integral is constant.

Stripped of its mathematical sophistication, Zermelo's argument is still elegant. A closed, adiabatic container limits the positions and velocities available to the molecules. Thus the number of positions in the phase space of this system is finite. Eventually, a system changing from one set of coordinates into a new set will run out of unused arrangements. It must now enter an arrangement it used before. The laws of dynamics now force the system to follow the same path through the different arrangements. The system must cycle.

Zermelo chooses as his example $n = 3$, which, he said, would form "stream lines" or "pipes" through phase space. The system could not escape from these pipes and each pipe leads back into itself.

In the derivation, Zermelo carefully and explicitly eliminates translations of the center of mass, molecules flowing into cavities and around solid objects. No broken light bulbs or open perfume bottles allowed. He admits the possibility of irreversible changes but comments,

> If we have a gas confined in an adiabatic container there is an unending variety of initial states in which the gas undergoes friction, heat conduction, or diffusion. On the other hand there are far more, equally likely initial states,...which inspite of such processes, periodically repeat....it is impossible...to carry out a mechanical derivation of the second law. Just as it is impossible, using the same assumptions, to derive a velocity distribution as a stationary final state.

REPLY TO THE CONSIDERATIONS ON THE THEORY OF HEAT OF ZERMELO

"The paper only shows that my pertinent works have not been understood" wrote Boltzmann in reply to Zermelo.[11] "Nevertheless" he continued "the paper made me happy since it is the first evidence that my work has been noticed in Germany at all. I have repeatedly stressed...that Maxwell's velocity distribution is not a law of the usual mechanics. It cannot be derived from the equations of motion alone." Later he adds, "The theorem of Poincaré...is obviously correct. Its application to the theory of heat is not." Throughout the paper Boltzmann argues that differences in degree make for differences in kind. Zermelo let $n = 3$ while Boltzmann's value for n approaches infinity.

Early in his paper Boltzmann describes his H function. "To a certain extent the amount the velocity distribution of a system deviates from Maxwell's." Plotting H against time for "a very large number" of molecules gives a curve with the value of H asymptotically approaching a low value H_{min}. Extending time or reducing the number of molecules puts "bumps" in the curve. The bigger the bump the smaller its probability. Boltzmann freely admits that given an infinite amount of time, another H value as high or even higher than the original would occur, not with the same positions of the molecules but with the same entropy value. In this sense the H curve is periodic. Then, in the last sentence of the paragraph, Boltzmann agrees that the original arrangement of molecules would recur.

Boltzmann did not give up the fight, however. He demands of Zermelo that his recurrence be something that takes place in "observable time." In an appendix Boltzmann calculates the length of time needed for a 1-cm^3 cube of gas to cycle. He finds the results of his calculation "reassuring." The number of seconds needed for a cycle has "many trillions of places." "If all of the stars visible with the best telescopes were circled by the same number of planets as our sun; and each of these planets had as many people as our earth; and if each of these people lived a trillion years...then all of the seconds experienced by all of the people would have fewer than 50 places."

In scattered places, Boltzmann describes the nature of Maxwell's velocity distribution. Throwing a die 6000 times results in an equal number of ones, twos, threes, etc., not because the particular number order is any more likely than getting 6000 ones. Equal numbers occur because of all the possible combinations the vast majority consists of approximately equal representations of the numbers. While Zermelo maintains that the number of states leading to Maxwell's distribution is small, Boltzmann claims that Maxwell's distribution describes the overwhelming number of states.

The return of an initial condition is still a nagging possibility. Boltzmann mentions that there are many possible events with a small probability that we do not expect to occur. A mixture of hydrogen and oxygen at room temperature has some molecules colliding with enough energy to form water. "We do not, however, find water." It is possible, he continues with a second example, that no air molecules strike a certain area causing a noticeable change in pressure. "We are not surprised when this does not occur." Boltzmann is quick to point out that for smaller systems, large deviations are possible—indeed the smaller system, the larger the possibility of deviation.

Boltzmann compares Zermelo to the dice player, who having learned that getting 600 snake eyes in a row is possible, thinks his dice are loaded because such an outcome never happened to him.

Boltzmann also mentions that Zermelo has described what we would call a thought experiment. The perfectly isolated system with perfectly smooth walls in Zermelo's experiment does not exist. "Disturbances could come from the electrical properties of the atoms, or, passed on to the atom through disturbances in the light ether."

Boltzmann flirts with, then rejects, cosmological considerations. He refused to speculate on why the earth is currently in such an unlikely state. Boltzmann then points out that one conclusion from the theory of Poincaré would be the return of the entire universe to its original state. This he dismisses as "beyond proof." "How can we decide if the length of time allotted to the universe is infinite or if the number of molecules is?" Boltzmann finds that speculating about the nature of the universe predicted by Poincaré's theorem is as barren as the thought that the second law will lead "after all irreversible processes have been played our" to "a universe where nothing happens or disappears for lack of occurrences."

CONCERNING MECHANICAL EXPLANATIONS OF IRREVERSIBLE PROCESSES: AN ANSWER TO BOLTZMANN'S "REPLY"

Zermelo[12] opens his answer to Boltzmann's reply much as he closed his first paper, "mechanical systems are periodic...and therefore not irreversible." He reasserts his faith in the second law, which was deduced from experiment, over a theory that lacks any direct proof. Boltzmann's ideas would, claims Zermelo, degrade the second law into a "simple law of probability valid only for a limited time." Zermelo admits, however, that Boltzmann is correct in stressing that the enormous number of molecules puts the Poincarean period beyond observation.

Zermelo's argument has changed, however. No longer does he rely on the return to a specific state with each molecule in the same place. A return to the exact state is not needed. As Boltzmann pointed out, all that must return is a physical state of equally low entropy.

The argument for the return no longer rests on the certainty of running out of virgin phase space, it has become probabilistic. Zermelo proved that all states have the same area and thus have the same probability of occurring. Even high H value, low entropy, states have a chance of appearing, and if one waits long enough, will.

Zermelo jumps on Boltzmann's admission that the H curve can occasionally reach new maximas and then return to a low value. "It does not suffice" claims Zermelo, "to show that all disturbances finally return to a long standing equilibrium." In order to reflect the second law the H function must "always decrease."

Zermelo gives the argument a new twist. He understands Boltzmann as claiming that his H curve usually falls from an initial maximum. In a mechanical system, state follows state. Suppose we choose as an initial state any later state. Zermelo has Boltzmann assuming that here too the H curve would fall from a maximum. The constantly changing H curve must consist of nothing but maxima. "Absurd" finds Zermelo.

Zermelo introduces his own version of the reversing paradox. Probability does not contain temporal terms. Therefore, Zermelo claims, probability cannot "determine the direction of events." We could, at least as far as probability is concerned, interchange the beginning and the end.

Picking up on Boltzmann's comment on the current unlikely state of the universe, Zermelo has a second argument. In any curve repeatedly returning to a maxima, every rise must have its fall. Thus, Zermelo finds, rises must be as likely as falls. Why, then do we never see the rising part of the H curve. Large numbers are now on Zermelo's side. He points out that entropy does not measure a single event. It is unlike, for instance, the eccentricity of the Earth's orbit. Here we could see only the rising or falling part of what is really a periodic curve. "We are concerned," Zermelo reminds us, "with the entropy of every conceivable system." Why, he asks, "with so many things to observe, do we only see the increasing side of entropy?"

Zermelo returns Boltzmann's dice player analogy. "Assume that a die gives 200 ones on the first 600 rolls, fewer on the next 600, and finally 100 ones for 600 rolls." One player, Zermelo tells us, would find nothing wrong since probability theory is valid only after many rolls. Another player finds that the die was loaded and only became fair after being worn down. Zermelo agrees with the second player.

REPLY TO ZERMELO'S ESSAY "CONCERNING MECHANICAL EXPLANATIONS OF IRREVERSIBLE PROCESSES"

Boltzmann[13] in the last paper in the series promises to "repeat the arguments as briefly as clarity will allow." One of the points he repeats is the inexact nature of probability. "If 100 out of 100,000 objects burn up in a given year we cannot conclude that 100 will burn up next year. On the contrary, if we continue the conditions for $10^{10^{10}}$ years, it could happen that all 100,000 burn in one day, or that none burn in an entire year. In spite of these difficulties, insurance companies trust probability theory."

Most of the paper deals with the state of the universe. "The 2nd law can be explained mechanically by the unprovable assumption that...the universe is in an improbable state." Any system which is isolated from the universe is likely to be in that improbable state and must be considered an arbitrary system. This, Boltzmann tells us, is why the H curve lowers, entropy increases, temperature and concentrations differences disappear, and the beginning and the end are not interchangeable.

We have a choice of explanations for this improbable universe, Boltzmann tells us. Either the universe in its entirety is in this improbable state or we are in a very improbable part of an otherwise dead universe. In a universe stilled by heat death, decreases in entropy would be as likely as increases. Tiny patches which greatly deviate from equilibrium can still exist "for the short space of aeons."

For the dead universe as a whole, both directions of time would be equally likely, Boltzmann adds, "just as in space there is no up or down." In centers of increasing entropy time would move as it does on earth, just as on the surface of the earth, down is toward the center. In patches of decreasing entropy, time would be reversed.

"Indulge in such speculations according to your taste," advises Boltzmann. "It does not affect the mechanical view of nature. I have asserted only that the mechanical view agrees with all observations. Hypothetical discussions on the nature of the universe or motion in a completely isolated system cannot upset the mechanical view."

CONCLUSION

Boltzmann's words did not end the discussion. Like the phenomenon it predicts, the recurrence paradox keeps coming back. Even high school physics texts[14] mention Zermelo's criticism in a discussion of Boltzmann's explanation of entropy. Whether to deny that God plays dice or to discern the end of the world, speculations on the nature of the universe are to many people's taste.

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Bound states, virtual states, and nonexponential decay via path integrals

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(Received 1 October 1982; accepted for publication 22 December 1982)

Using path integral techniques we demonstrate how three quantum-mechanical phenomena—alpha decay, nonexponential decay, and resonant scattering—can be treated. This procedure is an algebraic one yet reproduces the usual results obtained via solution of the Schrödinger equation via WKB methods.

Recently, in a pair of papers, we have shown how WKB results may be obtained via methods based upon the Feynman path integral.[1] This is advantageous from a pedagogical point of view for at least two reasons. First, one can perform these calculations without ever solving any differential equations or utilizing the "mysterious" WKB connection formula. Second, the use of path integral techniques has become an essential element of modern field theory and it is therefore useful to introduce students to these methods.

We have speculated that any problem solvable via WKB may be equally well solved using simple path integrals and have demonstrated this in the case of simple barrier penetration and transmission through the so-called double hump well.[2] In this note we wish to apply path integral techniques to the problem of alpha decay. As will be seen, we shall again be able to perform the calculation in a fairly simple way, which we think is of pedagogical value.

Our previous work has dealt with calculations of the propagator function

$$G(x_2,x_1;E) = \int_0^\infty \frac{dt}{2\pi\hbar} e^{iEt/\hbar}\langle x_2|e^{-iHt/\hbar}|x_1\rangle = \left\langle x_2\left|\frac{i}{E-H+i\epsilon}\right|x_1\right\rangle\frac{1}{2\pi} \quad (1)$$

