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On the Relation of a General Mechanical Theorem to the Second Law of Thermodynamics *

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SUMMARY

Loschmidt has pointed out that according to the laws of mechanics, a system of particles interacting with any force law, which has gone through a sequence of states starting from some specified initial conditions, will go through the same sequence in reverse and return to its initial state if one reverses the velocities of all the particles. This fact seems to cast doubt on the possibility of giving a purely mechanical proof of the second law of thermodynamics, which asserts that for any such sequence of states the entropy must always increase.

Since the entropy would decrease as the system goes through this sequence in reverse, we see that the fact that entropy actually increases in all physical processes in our own world cannot be deduced solely from the nature of the forces acting between the particles, but must be a consequence of the initial conditions. Nevertheless, we do not have to assume a special type of initial condition in order to give a mechanical proof of the second law, if we are willing to accept a statistical viewpoint. While any individual non-uniform state (corresponding to low entropy) has the same probability as any individual uniform state (corresponding to high entropy), there are many more uniform states than non-uniform states. Consequently, if the initial state is chosen at random, the system is almost certain to evolve into a uniform state, and entropy is almost certain to increase.

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In his memoir on the state of thermal equilibrium of a system of bodies with regard to gravity, Loschmidt has stated a theorem that casts doubt on the possibility of a purely mechanical proof of the second law. Since it seems to me to be quite ingenious and of great significance for the correct understanding of the second law, yet in the cited memoir it has appeared in a more philosophical garb, so that many physicists will find it rather difficult to understand, I will try to restate it here.

If we wish to give a purely mechanical proof that all natural processes take place in such a way that

$$\int \frac{dQ}{T} \leqq 0$$

then we must assume the body to be an aggregate of material points. We take the force acting between these points to be a function of the relative positions of the points. When this force is known as a function of these relative positions, we shall say that the law of action of the force is known. In order to calculate the actual motion of the points, and therefore the state variations of the body, we must know also the initial positions and initial velocities of all the points. We say that the initial conditions must be given. If one tries to prove the second law mechanically, he always tries to deduce it from the nature of the law of action of the force without reference to the initial conditions, which are unknown. One therefore seeks to prove that—whatever may be the initial conditions—the state variations of the body will always take place in such a way that

$$\int \frac{dQ}{T} \leqq 0$$

We now assume that we are given a certain body as an aggregate of certain material points. The initial conditions at time zero shall be such that the body undergoes state variations for which

$$\int \frac{dQ}{T} \leqq 0$$

We shall show that then, without changing the law of force, other initial conditions can be found for which conversely

$$\int \frac{dQ}{T} \geqq 0$$

Consider the positions and velocities of all the points after an arbitrary time t_1 has elapsed. We now take, in place of the original initial conditions, the following: all the material points† shall have the same initial positions at time zero that they had after time t_1 with the original initial conditions, and the same velocities but in the opposite directions. For brevity we shall call this state the one opposite to that previously found at time t_1.

It is clear that the points will pass through the same states as before but in the reverse order. The initial state which they had previously had at time zero, will now be reached after time t_1 has elapsed. Whereas previously we found

$$\int \frac{dQ}{T} \leqq 0$$

this quantity is now $\geqq 0$. The sign of this integral therefore does not depend on the force law but rather only on the initial conditions.‡ The fact that this integral is actually $\leqq 0$ for all processes in the world in which we live (as experience shows) is not due to the nature of the forces, but rather to the initial conditions. If, at time zero, the state of all material points in the universe were just the opposite of that which actually occurs at a much later time t_1, then the course of all events between times t_1 and zero would be reversed, so that

$$\int \frac{dQ}{T} \geqq 0$$

† By this we mean all the points of all bodies interacting with the one considered, either directly or indirectly. Strictly speaking one has to include all the points in the universe, since a complex of bodies that does not interact at all with the other bodies in the universe cannot actually be found, even though we can imagine it.

‡ It need not be mentioned that if the forces act in such a way that this is not true, for example if they are dynamical, then the following also loses its applicability.

Thus any attempt to prove from the nature of bodies and of the the force law, without taking account of initial conditions, that

$$\int \frac{dQ}{T} \leqq 0$$

must necessarily be futile. One sees that this conclusion has great seductiveness and that one must call it an interesting sophism. In order to locate the source of the fallacy in this argument, we shall imagine a system of a finite number of material points which does not interact with the rest of the universe.

We imagine a large but not infinite number of absolutely elastic spheres, which move in a closed container whose walls are completely rigid and likewise absolutely elastic. No external forces act on our spheres. Suppose that at time zero the distribution of spheres in the container is not uniform; for example, suppose that the density of spheres is greater on the right than on the left, and that the ones in the upper part move faster than those in the lower, and so forth. The sophism now consists in saying that, without reference to the initial conditions, it cannot be proved that the spheres will become uniformly mixed in the course of time. For the initial conditions which we originally assumed, the spheres will be almost always uniform at time t_1, for example. We can then choose in place of the original initial conditions the distribution of states which is just the opposite of the one which would occur (in consequence of the original initial conditions) after time t_1 has elapsed. Then the spheres would sort themselves out as time progresses, and at time t_1 they would acquire a completely non-uniform distribution of states, even though the initial distribution of states was almost uniform.

We must make the following remark: a proof, that after a certain time t_1 the spheres must necessarily be mixed uniformly, whatever may be the initial distribution of states, cannot be given. This is in fact a consequence of probability theory, for any non-uniform distribution of states, no matter how improbable it may be, is still not absolutely impossible. Indeed it is clear that any individual uniform distribution, which might arise after a certain time from some particular initial state, is just as improbable as an individual non-uniform distribution; just as in the game of Lotto, any individual set of five numbers is as improbable as the set 1, 2, 3, 4, 5. It is only because there are many more uniform distributions than non-uniform ones that the distribution of states will become uniform in the course of time. One therefore cannot prove that, whatever may be the positions and velocities of the spheres at the beginning, the distribution must become uniform after a long time; rather one can only prove that infinitely many more initial states will lead to a uniform one after a definite length of time than to a non-uniform one. Loschmidt's theorem tells us only about initial states which actually lead to a very non-uniform distribution of states after a certain time t_1; but it does not prove that there are not infinitely many more initial conditions that will lead to a uniform distribution after the same time. On the contrary, it follows from the theorem itself that, since there are infinitely many more uniform than non-uniform distributions, the number of states which lead to uniform distributions after a certain time t_1 is much greater than the number that leads to non-uniform ones, and the latter are the ones that must be chosen, according to Loschmidt, in order to obtain a non-uniform distribution at t_1.

One could even calculate, from the relative numbers of the different state distributions, their probabilities, which might lead to an interesting method for the calculation of thermal equilibrium.† In just the same way one can treat the second law. It is only in some special cases that it can be proved that, when a system goes over from a non-uniform to a uniform distribution of states, then $\int dQ/T$ will be negative, whereas it is positive in the opposite case. Since there are infinitely many more uniform than non-uniform distributions of states, the latter case is extraordinarily improbable and can be considered impossible for practical purposes; just as it may be considered impossible that if one starts with oxygen and nitrogen mixed in a container, after a month one will find chemically pure oxygen in the lower half and nitrogen in the upper half, although according to probability theory this is merely very improbable but not impossible.

† [Following up this remark, Boltzmann developed soon afterward his statistical method for calculating equilibrium properties, based on the relation between entropy and probability: *Wien. Ber.* **76**, 373 (1877).]

Nevertheless Loschmidt's theorem seems to me to be of the greatest importance, since it shows how intimately connected are the second law and probability theory, whereas the first law is independent of it. In all cases where $\int dQ/T$ can be negative, there is also an individual very improbable initial condition for which it may be positive; and the proof that it is almost always positive can only be carried out by means of probability theory. It seems to me that for closed paths of the atom, $\int dQ/T$ must always be zero, which can therefore be proved independently of probability theory. For unclosed paths it can also be negative. I will mention here a peculiar consequence of Loschmidt's theorem, namely that when we follow the state of the world into the infinitely distant past, we are actually just as correct in taking it to be very probable that we would reach a state in which all temperature differences have disappeared, as we would be in following the state of the world into the distant future. This would be similar to the following case: if we know that in a gas at a certain time there is a non-uniform distribution of states, and that the gas has been in the same container without external disturbance for a very long time, then we must conclude that much earlier the distribution of states was uniform and that the rare case occurred that it gradually became non-uniform. In other words: any non-uniform distribution evolves into an almost uniform one after a long time t_1. The one opposite to this latter one evolves, after the same time t_1, into the initial non-uniform one (more precisely, into the opposite of it). The distribution opposite to the initial one would however, if chosen as an initial distribution, likewise evolve into a uniform distribution after time t_1.

If perhaps this reduction of the second law to the realm of probability makes its application to the entire universe appear dubious, yet the laws of probability theory are confirmed by all experiments carried out in the laboratory.