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## THE BASIS OF THERMODYNAMICS

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March 1969

Ludwig Boltzmann, according to Viennese tradition, sometimes displayed a rather caustic wit. About philosophers he said once that he had found a lot of pertinent and correct comments in their writings, namely, as long as they criticized and abused other philosophers; the nonsense started only when they added something new on their own.

I hope that this paper will not be considered philosophical in the sense of Boltzmann, even if I say that a basis of thermodynamics has been missing so far, and that it must be epistemological.

There are two ways to look at the development of thermodynamics, the historical and the systematic. It is interesting enough to learn that thermodynamics has started from a technical problem, the efficiency of heat engines. A systematic investigation, however, can begin only after we notice that thermodynamics does not combine just mechanics and our knowledge of heat but that it extends into all branches of physical science. Conversely, we may describe the scope of thermodynamics as the knowledge of equilibrium and changes near equilibrium. Under this aspect it is clear that all physical sciences have their common root in thermodynamics and that they go their different ways as soon as problems of kinetics and dynamics arise. In each branch, equilibrium is a special case but this case is fundamentally the same in all branches. The basic ideas of thermodynamics are the basic ideas of science.

It is the wide scope of thermodynamics that imposes special requirements on the construction of its base. The simple, unconsidered transfer of mechanical concepts to other branches with ever new additions, patches and amendments obviously clashes with any claim of rigor. If we want a clear and clean structure of thermodynamics we must start from concepts that can be used in all physical sciences but do not depend on any of them. Conceptual cleanliness is of course a requirement indispensable for good teaching. But quite apart from didactic reasons I should not like to do without it.

The feeling of uneasiness in thermodynamics is as old as thermodynamics. Carathéodory as well as many other authors before and after him felt this uneasiness very strongly. Carathéodory introduced two important ideas into thermodynamics, which turned out to be the corner stones of its modern development. He also introduced axiomatics, which was elaborated to a tremendous extent by some later authors.

It was quite natural to believe that thermodynamics could be improved by strengthening its mathematical deductions. Actually, however, the mathematical derivations in thermodynamics have never presented very serious problems. The real difficulty has always been in the basic concepts. The axiomatists made a very great effort to build elaborate and complicated structures. Unfortunately equal care was not taken for selecting satisfactory construction materials, i.e., basic concepts.

Before we try to supply sound lumber for the thermodynamic structure, a few comments on the application of mathematics in physical science may be useful.

A quantity is defined by a prescription of how to measure it. Any measurement is a comparison with an arbitrarily chosen standard quantity. The essence of the prescription is the decision: greater, or equal, or smaller. The

definition is completed by the choice of the standard and the assignment of numbers (which can be arbitrarily changed by any monotonically increasing transformation). Since every measurement is affected by a finite error, the result is a rational number.

All this is well known. We jump from rational numbers into the field of real numbers in any kind of physical theory. Even a simple interpolation of experimental data by means of a straight line involves such a jump.

Falk and Jung (1959) drew the conclusion that in the introduction of basic variables continuity should not be postulated though they do not object to continuity and differentiability in any later step.

Perhaps we should go farther. In a strict way, the information content of our observations cannot be increased by the jump to real numbers. Actually we could set a computer for a field of thirty digits, and represent and apply the total of our knowledge in the denumerable field of this computer. The equivalent of differentiations, integrations and so on can be (and is) carried out by computers. All our scientific results and all technical applications could be delivered by such a computer.

The conclusion is simple. In physical science, questions of continuity are not real problems since continuity is introduced only for the convenience of abbreviated computation.

This matter is important because of Buchdahl's presentation of the second law. Buchdahl (1954) started from Carathéodory's principle, namely, the statement that in the neighborhood of any state there are other states inaccessible by adiabatic processes. The division into inaccessible, reversibly accessible, and irreversibly accessible states is the basis for the definition of the entropy, which is defined by this division just as any other quantity is.

Buchdahl (1962) later modified this presentation of the second law on the ground that it is not permissible for a continuous variable. The new presentation is complicated and difficult.

This example shows that the mathematical interpretation of observations, which has contributed so much to the progress of science, may also create pseudo-problems that we can dismiss prima facie.

Where do we find, now, the sound lumber for a solid structure of thermodynamics?

Several years ago, a book by the name of "Fundamental Theory" was very famous - for a short time. I could not find anything fundamental in it as soon as I noticed on the first page that the author had no qualms to use the concept of energy without any attempt to state what he means. Any "fundamental" discussion must start with introducing the concepts in a proper way. This means that we must describe them in plain, uncoded language without any recourse to a specific branch of science. We must, moreover, demonstrate their general applicability.

But how can this be done? This looks like the juggler's problem, namely, to climb upon his own head.

The simple solution of this problem will show that Boltzmann's harsh picture of philosophers is incorrect, at least as far as epistemology is concerned. From Kant's long and complicated discussions one can distil the plain comment that those concepts are generally applicable that are indispensable for expressing the results of our observations. This comment is simple but it has a long and involved history leading from Descartes to Hume, Berkeley and Kant. The picture of philosophers always tearing down the work of their predecessors and starting again from scratch is not just an oversimplification, it is plainly wrong.

In physical science, as distinguished, e.g., from history, we restrict ourselves to the description of reproducible events. A complete description includes, explicitly or silently, an instruction of the steps leading to a repetition of the event.

The description necessarily starts with a finite part of the world. We call it object if it can be isolated. Thus the ideas of an object and of isolation are coupled. An object is isolated if its properties remain unchanged whatever changes may occur in any other object (its environment).

The concept "isolation" (and therefore also that of an object) is an idealization. There is no perfect realization of such a requirement as isolation. The same situation we find at every step and we accept it without any repeated discussion. But the incomplete realization of such conditions limits, of course, the accuracy of our description.

Reproducibility presupposes our ability to change an object according to our pleasure. This is being done by establishing interaction between the object and some other object. It is easy to describe mechanical interaction, or the flow of an electric charge from one object to another, or a chemical reaction and so on. But if we want to establish the basis of thermodynamics we must furnish a general description of interaction. The description will indeed cover any kind of interaction except thermal interaction, which requires a separate discussion.

When we establish interaction between two otherwise isolated objects A and B, we impose a condition on at least one variable  $x'$  of A and a variable  $x''$  of B, variables that before were independent of each other. The nature of this condition



$$F(x', x'') = 0 \quad (1)$$

and the kind of interaction (mode of interaction) is determined by the tool or gadget used for establishing interaction (a clamp or a hook and eye, a couple of copper wires, a catalyst, and so on). Since we can replace a variable  $x$  by any monotonic function of  $x$ , we can always express the interaction condition (1) with the aid of a constant  $C$  as

$$x' + x'' = C \quad (2)$$

In general, but not necessarily, we use this form of the interaction condition. We call the variable  $x$  a generalized coordinate. No special concept of any branch of science has been used in its definition. Whatever  $x'$  is, by establishing interaction with a suitable second object we can change the first object so that  $x'$  assumes an arbitrarily prescribed value.

In general we must take into account more than a single independent variable  $x'$ . The number of possible non-thermal interactions is indefinite. But it has a finite value  $h$  for any specific problem that we choose to consider. Thus the requirement of reproducibility implies that the state of the object reach a prescribed point in an  $h$ -dimensional space. Each of the  $h$  interaction conditions (1) would contain all  $h$  variables  $x'_j$  and all  $h$  variables  $x''_j$ . Moreover, the next problem we wish to consider for the same object may involve different modes of interaction and therefore require some different variables.

An orderly description of the object can be attained only by means of an orthogonality condition. Each generalized coordinate must be chosen so that it varies only if a specific mode of interaction (the conjugate mode) takes

place and that it stays constant while any other interactions are going on. In other words, every coordinate is fixed as long as the object is isolated with respect to its conjugate mode of interaction.

With this choice of coordinates we can attain any state, characterized by  $h$  coordinates, simply by establishing in turn  $h$  interactions and changing one coordinate to the prescribed value in each of the  $h$  steps.

In the interaction described by (2) the change  $dx'$  of  $x'$ , after interaction has been established, can be negative, zero, or positive. The observation of this change realizes a Dedekind cut that defines the generalized force  $f$  by means of the statements

$$f' > f'' ; f' = f'' ; f' > 0 \quad (3)$$

for the three cases. As every quantity, the force is measured by comparison with a standard quantity, i.e., a standard force (weight of a certain piece of platinum). But an important distinction of any generalized force (and the temperature) from any other quantity in nature rests on the fact that we have to establish equilibrium between the object and the standard object (gauge) if we want to measure a force directly. This very simple, though previously unknown, distinction follows directly from the definition of a generalized force.

The substance of the present system of concepts does not depend on any appeal to special observations. It is developed as a coherent procedure of gathering orderly information of things and events that can be reproduced. It is clearly applicable to any conceivable interaction near equilibrium.

In the last one hundred years several authors noticed that the variables now called generalized coordinates and forces belong to two classes, differing from each other and from all other variables. But repeated attempts to characterize these classes were unsuccessful. Consequently the concept of work, defined as the integral of a generalized force with respect to its generalized coordinate, never had a solid foundation.

On the basis of the present discussion, work can be introduced in a clear and unambiguous manner. Temperature can be defined in the conventional way. The path to the first and second law has been shown by Carathéodory.

Serious mistakes have been the curse of thermodynamics. They have caused the uncertainty and uneasiness that often have emerged. They have been repressed by the habit-forming procedures of applying thermodynamics. Wrong definitions of extensive and intensive quantities, of generalized coordinates and forces, and defective definitions of work have been quite common. A historical accident, namely, Tolman's unawareness of a prior definition, has greatly contributed to a widespread confusion of extensive and intensive quantities with coordinates and forces. The so-called zeroth law, going back to Carathéodory, is not only unnecessary but actually misleading.

The problems of the relationship between the physical sciences and mathematics become more manifest in thermodynamics than in any other part of science. The wonderful efficiency and elegance of so many mathematical tools, starting from the concept of the limit, should not induce us to see in them more than tools. The theoretician as well as the experimenter must be the master of his tools, not their slave.

It has been the purpose of the present discussion to show that thermodynamics can be developed in a clear and consistent conceptual structure. We may conclude that thermodynamics can be understood.

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