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TEACHING ENERGY AND ENTROPY
BEFORE TEMPERATURE AND HEAT
NOT VICEVERSA

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1. Introduction.

In many expositions of thermodynamics, the concept of heat is introduced at the outset of the logical development in terms of mechanical illustrations aimed at demonstrating the difference between heat and work.

For example, in his lectures on physics, Feynman[1] describes heat as one of several different forms of energy related to the jiggling motion of particles stuck together and tagging along with each other (pp. 1-3 and 4-2), a form of energy which really is just kinetic energy—internal motion (p. 4-6), and is measured by the random motions of the atoms (p. 10-8). Tisza[2] argues that such slogans as “heat is motion,” in spite of their fuzzy meaning, convey intuitive images of pedagogical and heuristic value.

There are at least two problems with these illustrations. First, work and heat are not stored in a system. Each is a mode of transfer of energy from one system to another. Second, and perhaps more important, concepts of mechanics are used to justify and make plausible a notion—that of heat—which is beyond the realm of mechanics. In spite of these logical drawbacks, the trick

works because at first the student finds the idea of heat harmless, even natural. But the situation changes drastically as soon as the notion of heat is used to define a host of new ideas, less natural and less harmless. At once, heat is raised to the same dignity as work, it is contrasted to work and used as an essential ingredient in the first law. The student begins to worry because the notion of heat is less definite than and not as operational as that of work.

The first problem is addressed in some expositions. Landau and Lifshitz[3] define heat as the part of an energy change of a body that is not due to work done on it. Guggenheim[4] defines heat as an exchange of energy that differs from work and is determined by a temperature difference. Keenan[5] defines heat as that which transfers from one system to a second system at lower temperature, by virtue of the temperature difference, when the two are brought into communication. Similar definitions are adopted in notable textbooks, such as Van Wylen and Sonntag[6], Wark[7], Huang[8], Modell and Reid[9], and Moran and Shapiro[10].

None of these definitions, however, addresses the basic problem. The existence of exchanges of energy that differ from work is not granted by mechanics. It is one of the striking results of thermodynamics, that is, of the existence of entropy as a property of matter. Hatsopoulos and Keenan[11] have pointed out explicitly that without the second law heat and work would be indistinguishable and, therefore, a satisfactory definition of heat is unlikely without a prior statement of the second law.

In our experience, whenever heat is introduced before the first law, and then used in the statement of the second law and in the definition of entropy, the student cannot avoid but sense ambiguity and lack of logical consistency. This results in the wrong but unfortunately widely spread conviction that thermodynamics is a confusing, ambiguous, hand-waving subject.

During the past twenty years of teaching thermodynamics to students from all over the globe, we have sensed a need for more clarity, unambiguity and logical consistency in the exposition of thermodynamics than provided by traditional approaches.

Continuing the effort pioneered by Keenan and Hatsopoulos, we have composed an exposition[12] in which we strive to develop the basic concepts without ambiguities and logical inconsistencies, building upon the student's sophomore background in introductory physics.

The basic concepts and principles are introduced in a novel sequence that eliminates the problem of incomplete definitions, and that is valid for both macroscopic and microscopic systems, and for both equilibrium and nonequilibrium states. The laws of thermodynamics are presented as fundamental laws of physics that complement the laws of dynamics. Heat plays no role in the first law, the definition of energy, the second law, the definition of entropy, and the concepts of energy and entropy exchanges between interacting systems. It emerges as a consequence of these concepts and laws. Heat is the energy exchanged between systems that interact under very restrictive conditions that define what we call a heat interaction.

In this paper we summarize and illustrate the key aspects of the novel logical sequence that we propose in our exposition of the foundations of thermodynamics. We emphasize that although this exposition makes no reference to the ideas of Quantum Thermodynamics it is construed so as to be entirely compatible with it, particularly in the general aspects concerning the definition of entropy for nonequilibrium states.

2. The logical sequence of the new exposition.

We outline briefly the logical sequence of our detailed exposition of the foundations of thermodynamics in Ref. 12. We do this not only to show in which way it is possible to present the laws of thermodynamics without resorting to heuristic definitions of heat and temperature, but also to emphasize that this is done by building gradually upon the sophomore background in physics, thus providing continuity in the development of a

student's understanding of natural phenomena.

We begin with kinematics and dynamics. In kinematics, we discuss the definitions of system, property, and state. The concept of state that we define provides the common thread for the unification of the various branches of physics without need to modify its meaning from branch to branch. The state is the set of instantaneous values of all the amounts of constituents, all the parameters that characterize the external forces, and all the properties. Without alteration, this definition is valid for any system, macroscopic or microscopic, and any condition, changing or not changing with time.

In dynamics, we discuss spontaneous and induced changes of state as functions of time, i.e., we introduce the idea of the equation of motion of a system. Certain time evolutions obey Newton's equation of motion or its quantum-mechanical equivalent—the Schrödinger equation of motion. Other experimentally observed time evolutions, however, do not obey either of these equations. So the equations of motion that we have are incomplete. The discovery of the complete equation of motion that describes all physical phenomena remains a subject of research at the frontier of science—one of the most intriguing and challenging problems in physics. Among the many features that have already been discovered, the most general and well established are captured by the statements of the first law and the second law of thermodynamics. We note that from these two laws derive the most powerful tools to investigate time dependent phenomena.

We introduce a carefully worded and unambiguous statement of the first law in terms of the concept of state and the definition of a weight process. We show that one of the principal implications of this statement is the existence of the property that we call energy and denote by E . Energy is defined for all systems and all states, and is an additive property. It obeys a conservation principle, i.e., it remains invariant in the course of spontaneous changes of state of an isolated system. Because changes of state require a finite time to occur, the principle of energy conservation

implied by the first law is an aspect of time evolution. As such, it reflects a special feature of the general equation of motion, even though the equation itself remains to be discovered.

Other implications of the first law are the impossibility of a perpetual motion machine of the first kind, the relation of the law to relativity and mass, and the energy balance. The energy balance is the most universal and powerful tool used in the analysis of practically every physical phenomenon.

Next, we recognize that at a given instant of time a system can be found in one of many different states. We classify each state according to its time evolution, and define unsteady, steady, nonequilibrium, unstable equilibrium, metastable equilibrium, and stable equilibrium states.

We recall that equilibrium is not always stable, and raise the question: "Among all the states of a system that correspond to a given value of the energy, are there any that are stable equilibrium?" Close scrutiny of this question reveals that the answer cannot be found by means of the theory of mechanics. And yet experience shows that such stable equilibrium states exist. The answer is provided by the second law of thermodynamics.

We introduce a carefully worded and unambiguous statement of the second law in terms of the concepts of energy, stable equilibrium state, and reversible process. This statement is an outgrowth of the pioneering work by Hatsopoulos and Keenan. In due course we show that our statement entails all correct statements of the second law that have appeared in the literature. We emphasize that the second law implies the existence of stable equilibrium states but does not require that all states be stable equilibrium. Indeed, the vast majority of states are nonequilibrium. The requirement that some equilibrium states must be stable reflects a most important feature of the general equation of motion, even though this equation remains to be discovered.

The two laws of thermodynamics have many important and practical implications. One of these implications, is the impossibility of a perpetual motion machine of the second kind.

Another is that, in general, not all the energy of a system can be transferred to a weight in a gravity field. Under the broad restrictions that define a weight process, the amount of energy that can be transferred from a system to a weight depends on the state of the system. If it is not a stable equilibrium state, at least a fraction of the energy can be transferred to the weight. But, if it is a stable equilibrium state, no energy can be transferred to the weight. This limitation reflects innumerable experimental observations, but cannot be accounted for by the principles of mechanics alone. It is one of the important implications of the two laws of thermodynamics.

We prove the existence of a novel important property that we call adiabatic availability and denote by Ψ . The adiabatic availability of a system in a given state is related to the optimum amount of energy that can be exchanged between the system and a weight in a weight process. Like energy, this property is well defined for all systems and all states. Unlike energy it is not additive.

In striving to define an additive property that captures the important features of adiabatic availability, we introduce a special reference system, called a reservoir, and discuss the possible weight processes that the composite of a system and the reservoir may experience. We prove the existence of another important property that we call available energy with respect to a given reservoir, and denote by Ω^R . The available energy of a system in a given state is the adiabatic availability of the composite of the system and the reservoir. It is a generalization of the concept of motive power of fire first introduced by Carnot. Like energy and adiabatic availability, it is a well defined property for all systems and all states, but depends on the reference reservoir.

Finally, we disclose the existence of the property that we call entropy, and denote by S . Entropy is defined in terms of energy, available energy with respect to an arbitrarily selected reservoir, and a constant that depends on the reservoir. In terms

of symbols the definition is

$$S = S_o + \frac{1}{c_R} [(E - E_o) - (\Omega^R - \Omega_o^R)]$$

where E_o and Ω_o^R refer to an arbitrary reference state, S_o is a constant fixed once and for all for the system, and the constant c_R is a carefully defined property of the reservoir. We prove that the role of the reservoir is only auxiliary, i.e., that the value of S is independent of any characteristics of the arbitrarily selected reservoir. Because both E and Ω^R are defined for all systems (macroscopic as well as microscopic) and all states (equilibrium as well as nonequilibrium), S is also defined for all systems and all states, including a system with one degree of freedom in any of its states.

The concept of entropy introduced here differs from and is more general than that of most textbooks where, as Callen[13] stresses, the existence of the entropy is postulated only for equilibrium states and the postulate makes no reference whatsoever to nonequilibrium states.

We show that entropy obeys a principle of nondecrease, i.e., it either remains invariant or increases in the course of spontaneous changes of state of an isolated system. We show that a spontaneous process is irreversible if the entropy increases, and we call such increase a creation or generation of entropy within the system. Like the principle of energy conservation, the principle of nondecrease of entropy is an aspect of the time evolution and, as such, it reflects another special feature of the general equation of motion that remains to be discovered. We finally introduce the entropy balance which is another powerful tool for analyses of physical phenomena.

At this stage of our exposition, energy and entropy are fully and rigorously defined for equilibrium as well as nonequilibrium states. The concepts of temperature and heat have not yet been either defined or used. As already emphasized, this fact is a most distinguishing feature of our exposition of thermodynamics.

Next we focus our attention on the stable equilibrium states. We show that at a stable equilibrium state the value of any property is fully and uniquely determined by the values of the energy, the amounts of constituents, and the parameters. This conclusion is known as the state principle. It is reached without any extraneous considerations, such as lack of information, difficulty associated with complicated calculations, unpredictability of initial conditions, or lack of interest in making detailed analyses of large systems.

We derive the highest entropy principle and the lowest energy principle as useful criteria for stable equilibrium. We discuss a special form of the state principle known as the fundamental relation. It avers that the value of the entropy at a stable equilibrium state is uniquely determined by the values of the energy, the amounts of constituents, and the parameters. Again, this is a rigorous and general result, involving no approximation whatsoever.

We use the highest entropy principle to investigate necessary conditions that must be satisfied for two systems to be in mutual stable equilibrium, i.e., for the combination of the two systems to be in a stable equilibrium state. These investigations disclose the existence of properties that are defined only for stable equilibrium states, namely, temperature, total potential of a constituent, and pressure. Each of these properties is defined in terms of a partial derivative of the fundamental relation, and is readily measurable. More importantly, we show that necessary conditions for systems to be in mutual stable equilibrium are temperature equality, total potential equality for each constituent, and pressure equality. Each of these equalities provides the theoretical foundation for the measurement of the respective property.

At this stage, we are finally ready to introduce work and heat interactions. A work interaction is defined by the condition that its result be a net exchange of energy between the interacting systems involving no exchange of entropy. We call nonwork any interaction that is not work. A heat interaction is only a special nonwork interaction.

A heat interaction is defined by the condition that it be entirely distinguishable from work—no part of a heat interaction be mistakable as a work interaction. We prove that such an interaction exists, results in a net exchange of both energy and entropy, requires that the interacting systems be almost at the same temperature, and is such that the ratio of the amount of energy exchanged to the amount of entropy exchanged equals the almost common temperature of the interacting systems.

We discuss the energy balance and the entropy balance for a system experiencing only work and heat interactions. The change in energy equals the sum of the work and the heat to the system. This result is just a very special consequence of the two laws of thermodynamics and, hence, cannot be called “the first law”. The change in entropy equals the entropy supplied by the heat interaction plus the entropy generated spontaneously by irreversibility within the system. Also this result is just a very special consequence of the two laws of thermodynamics and, hence, cannot be called “the second law”.

Work and heat are ingenious concepts. For given end states of a system, they allow the quantitative distinction between entropy generated by irreversibility and entropy exchanged via interactions with other systems. As such, these two concepts provide practical means for identifying opportunities to reduce the entropy generation by irreversibility and, hence, improve the performance of the system. The identification of these opportunities would be missed if heat were defined as just any interaction that is not work, i.e., any nonwork interaction.

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