DEDUCTIVE QUANTUM THERMODYNAMICS

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The purpose of this paper is to summarize the main ideas and some of the conclusions of a physical theory in which the second law of thermodynamics is presented as an unavoidable and independent part of the fundamental postulates of physics. The detailed exposition of the theory is given in Reference [1].

For more than a century the relations between mechanical and thermodynamic properties, as they have been investigated by means of statistical methods, have been the subject of controversy. During this time, a number of statistical thermodynamic theories have been advanced. Initially, these theories were based on Newtonian mechanics, later on the principles of quantum mechanics.

A characteristic of all statistical theories is that they yield the same results for stable states of systems having sufficiently large numbers of degrees of freedom. On the other hand, they yield significantly different results when applied to systems having a small number of degrees of freedom, or to systems of any kind in nonstable states. Moreover, in general, there are important conceptual differences between different theories. For example, Gibbs [2], Pauli [3], Klein [4], and Jaynes [5] differ in the explanation of irreversibility, and in the general expression for entropy.

Existing statistical theories are based on the reversible laws of mechanics supplemented by additional postulates such as ergodicity, or equal *a priori* probabilities, or information theory. In each theory, a quantity is found, which for an isolated system cannot decrease, at least initially, but which may increase, at least for a while. This quantity is assumed to represent the entropy of the system. In each case, the assumption is justified by the fact that the results of the theory are consistent with those predicted by the laws of classical thermodynamics for stable states and for changes between such states.

If all that is required from a statistical theory is to yield, in the limit of stable equilibrium, results consistent with classical thermodynamics, then

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all existing theories would be equally correct. Such a requirement, however, is inadequate. For the second law of thermodynamics implies much more than relations between the properties and the change in the properties of systems passing through stable states. It implies, among other things, the existence of irreversible processes—that is, processes whose effects on all the systems involved cannot be undone. This implication must be taken literally. For example, the acceptance of the second law and its many corollaries necessitates unqualified acceptance of the conclusion that all the effects of an irreversible process cannot be undone no matter what sophisticated technology is employed, including measurements of properties either at a macroscopic or at a microscopic level. Otherwise, the second law would be as meaningless as saying that the expression for the Carnot efficiency of a heat engine is dependent upon technology, or economics, or the complexity of the engine, or saying that the Heisenberg uncertainty principle expresses no more than the accuracies that may be obtained with today's laboratory practices.

No statistical theory advanced so far proves the second law of thermodynamics or for that matter the existence of irreversible processes in the sense described. Probably none will ever prove it. Moreover, no theory has ever been derived which is completely consistent with the second law.

Reference [1] attempts to develop a theory consistent with the second law. The procedure used is as follows. The second law is stated as a fundamental postulate of physics. From this law and the postulates of quantum mechanics a theory is formulated that appears to be self-consistent. If the theory were not self-consistent this would mean that either the second law is not applicable or the laws of mechanics are not applicable to natural phenomena. Of the two alternatives, the evidence is overwhelmingly in favor of the selection of the second law as valid. For there is no recorded experiment in the history of science that contradicts the second law or its corollaries as stated in this paper. No such statement can be made about the known laws of mechanics.

The present theory, like all previous statistical theories, yields a general expression for the entropy of a system. This expression is applicable to all states, equilibrium or nonequilibrium, of all systems, with few or many degrees of freedom. Moreover, it is shown that the expression is *the only one* consistent with the second law and the laws of mechanics. The expressions of entropy given by Klein [4], Tolman [6], and Jaynes [5] are applicable only in special processes. The use of these expressions in other processes leads to the erroneous conclusion that they are irreversible (in the rigorous sense implied by the second law) when, in fact, they are not.

No arguments given in the present theory depend upon the number of degrees of freedom of the systems considered. It is true that systems with enormous numbers of degrees of freedom differ substantially from those with few degrees of freedom. The differences are, however, only quantitative

and not qualitative. Contrary to common opinion, not only are all the methods of thermodynamics applicable to systems with few degrees of freedom as well as to those with many degrees of freedom, but the exact thermodynamic analysis of a specific system may prove far easier when the number of degrees of freedom is small. This fact is demonstrated by a paper on the definition of electronegativity [7].

Some additional major conclusions in Reference [1] are as follows:

(a) The description of the condition of matter by means of a wave function is inadequate. This conclusion is similar to that arrived at half a century ago when it was recognized that, by virtue of the Heisenberg uncertainty principle, the classical description of matter is inadequate.

The rationale behind this conclusion may be illustrated by the consideration of two theorems, one from thermodynamics and one from quantum mechanics. It follows from the statement of the second law given in Reference [1] that in the vicinity of any state of a system there are states that cannot be reached by means of adiabatic processes. In fact, Carathéodory [8] used this theorem as his statement of the second law. On the other hand, it follows from the laws of quantum mechanics that any quantum-mechanical state described by a wave function may be connected to any other quantum-mechanical state also described by a wave function by means of an adiabatic process This theorem was proved by von Neumann [9]. The apparent contradiction between the two theorems may be reconciled in either of two ways. First, it may be assumed that the term "state of a system" in thermodynamics has a different meaning than the same term in mechanics. This explanation of the contradiction is the one prevailing in the literature. Second, the position may be taken that the term "state of a system" has the same meaning in both thermodynamics and mechanics, and that the second law indicates the existence of quantum-mechanical states which cannot be described by a wave function. The theory summarized herein is based on this position and, hence, the conclusion that a wave function is not adequate to describe all conditions of a system.

The condition of a system may be described in general by a linear Hermitian operator $\hat{\sigma}$ called the *coherence operator*. The operational definition of $\hat{\sigma}$ is as follows. The precise measurement of a property $\bar{F}$ (quantum-mechanical observable) yields the eigenvalue $F_{\alpha m}$ of the alpha component $\hat{F}(\alpha)$ of the operator $\hat{F}$ with a probability $\sigma_{\alpha m;\alpha m}$ given by the relation

$$\sigma_{\alpha m;\alpha m} = \int v^*_{\alpha m} \hat{\sigma} v_{\alpha m} \, dq,$$

where

$$\hat{F}(\alpha) v_{\alpha m} = F_{\alpha m} v_{\alpha m}.$$

The index α is used to denote the fact that, in general, quantum-mechanical operators $\hat{F}$ have components $\hat{F}(\alpha)$ that lie in different Hilbert spaces α.

(b) The unique expression for the entropy S is given by the relation

$$S = -k \operatorname{Tr} \left[\left[\sigma\right] \ln \left[\sigma\right]\right],$$

where k is Boltzmann's constant, $[\sigma]$ is the coherence supermatrix with elements $\sigma_{\beta m; \alpha n}$ given by the relation

$$\sigma_{\beta m; \alpha n} = \delta_{\alpha\beta} \int v^*_{\alpha m} \hat{\sigma} v_{\alpha n} \, dq,$$

and $\delta_{\alpha\beta}$ is the Kronecker delta.

(c) A system in stable state does not pass through a succession of states each of which is described by a wave function. It remains in that stable state (it is described by the same $[\sigma]$) as long as it is not disturbed by interactions with other finite systems. A finite system is defined as one for which the probabilities associated with the results of all possible measurements are not all zero.

In the context of the present theory, the ergodic hypothesis is meaningless.

(d) The measurement of an observable of a system in a stable state yields, in general, results that can be predicted probabilistically only. The same statement applies to a system in any other state, including one described by a wave function.

(e) Irreversibility in a finite system A can be attributed neither to interparticle collisions and correlations, nor to coarse graining and quantummechanical broadening. Any statements to the contrary violate the laws of quantum mechanics.

(f) Irreversibility in a finite system A cannot be attributed to interactions with another finite system B, irrespective of the nature of the interactions. Any statements to the contrary violate the laws of quantum mechanics.

(g) Irreversibility in a finite system A (a direct consequence of the second law) is due to interactions between A and another system that is nonfinite. A nonfinite system is defined as one for which the probabilities associated with the results of all possible measurements are all zero. An example of a nonfinite system is the "vacuum" of relativistic quantum field theory. This vacuum experiences only irreversible interactions with its finite system A.

(h) The present theory is probabilistic in the same sense that quantum mechanics is probabilistic. The theory is not statistical, however, in the sense of statistical mechanics.

(i) The procedures and conclusions of the paper appear to be of extremely general application.

REFERENCES

1. G. N. Hatsopoulos and E. P. Gyftopoulos, On the Implications of the Second Law of Thermodynamics in Quantum Theory, submitted for publication in Physical Review.

2. J. W. Gibbs, The Collected Works, Vol. II, Chap. XIV, Yale University Press, 1948.
3. W. Pauli, Sommerfeld Festschrift, p. 30, Leipzig, 1928.
4. O. Klein, Z. Physik. *72*, 767 (1931).
5. E. T. Jaynes, Phys. Rev. *108*, 171 (1957).
6. R. C. Tolman, The Principles of Statistical Mechanics, p. 536, Clarendon Press, 1938.
7. E. P. Gyftopoulos and G. N. Hatsopoulos, Proc. Natl. Acad. Sci. *60*, 3, 786 (1968).
8. C. Carathéodory, Grundlagen der Thermodynamik, Math. Ann. *67*, 355 (1909).
9. J. von Neumann, Mathematical Foundations of Quantum Mechanics, Chap. V, Princeton University Press, 1955.

Comments

I. Prigogine: The difficulty is that there exist initial states such that, at least over a period of time, the entropy of the system decreases (see my paper in this volume). For this reason, I do not see why a modification of Quantum Mechanics should be introduced in order to force agreement with macroscopic thermodynamics for all possible situations.

G. N. Hatsopoulos: The current view concerning physical systems is that the instantaneous state of a system is a quantum mechanical state that can be described by means of a wave function. Moreover, a thermodynamic state is viewed as an ensemble average of quantum mechanical states and operationally equilibrium states are interpreted as time averages of the states assumed by a system over long periods of time, or as averages over many experiments on systems prepared in some specified fashion.

Our point of view differs from the current view in the following way: We view a thermodynamic state as one that a system may assume at an instant of time. Mathematically, it can be described by a means of an operator $\hat{\sigma}$ which, in general, has components in many Hilbert spaces. Each Hilbert space corresponds to a given number of degrees of freedom and values of constraints. For example, different Hilbert spaces are required because particles may be created and annihilated.

Measurements of a dynamic variable, such as the energy, will yield various results for a given thermodynamic state—not because the system passes through different energy eigenstates as time goes on, but because the measurement disturbs the original state of the system. The probability that this or that result will be obtained from a measurement is uniquely determined by the operator $\hat{\sigma}$ describing the thermodynamic state prior to the measurement.

From some states, the operator $\hat{\sigma}$ is equivalent to a wave function. These are the zero entropy states. For other states, the operator $\hat{\sigma}$ is equivalent to a Von Neuman n density matrix operator $\hat{\rho}$. The operator $\hat{\sigma}$, however, can describe states that cannot be represented either by a wave function or by a density matrix. It is this feature of the theory that makes it consistent with the requirements of both quantum theory and those of the second law of thermodynamics.

For reversible processes only, the equation of motion of a system whose state is described by an operator σ is given in the paper. This equation becomes identical to that for Von Newman's density operator $\hat{\rho}$ for those states for which $\hat{\sigma}$ and $\hat{\rho}$ are equivalent.

For irreversible processes, the equation of motion is not known. Irreversible processes can occur only if the system in question is interacting with a system characterized by a nonfinite $\hat{\sigma}$. The vacuum of quantum field theory is an example of a nonfinite system.