

The Laws of Thermodynamics: A Necessary Complement to Quantum Physics

ELIAS P. GYFTOPOULOS

Massachusetts Institute of Technology, 77 Massachusetts Ave.,
Cambridge, MA 02139

GEORGE N. HATSOPOULOS

Thermo Electron Corporation, 101 First Ave., Waltham, MA 02154

The purpose of this paper is to discuss the hypothesis that the second law of thermodynamics and its corollaries are manifestations of microscopic quantum effects of the same nature but more general than those described by the Heisenberg uncertainty principle. This hypothesis is new to physics.

Energy is a property of matter that has unified our understanding of physical phenomena. It appears prominently in both mechanical and thermodynamic theories. It is defined by the first law of thermodynamics, and its conservation is one of the keystones of analyses of both microscopic and macroscopic phenomena.

Adiabatic availability--the amount of work that can be extracted from a system adiabatically--is also a property of matter but has not been accepted with the same unanimity as energy. Experience, especially with large bodies, indicates that not all the energy of a system is available in the form of work. For a given system, say atoms in a box, mechanics implies that all the energy (above the ground state) can be extracted adiabatically in the form of work, regardless of whether the system is large or small. In contrast, the second law of thermodynamics implies that not all the energy can be extracted in the form of work, namely that the adiabatic availability is smaller than the energy and that it can be even zero.

Though perhaps expressed in different terms, the contrast just cited has been the subject of intensive inquiry and controversy ever since the enunciation of the first and second laws of thermodynamics in the 1850's. Invariably, a reconciliation is proposed based on regarding thermodynamics as a statistical macroscopic or phenomenological theory.

We believe that such reconciliation is not adequate. Moreover, we believe that the thermodynamic behavior of matter is due to quantum uncertainties of the same nature but broader than those associated with wave functions and invoked in the uncertainty principle.

In what follows, we discuss the current interpretation of the relation between thermodynamics and microscopic structure of

matter, the accepted representation of quantum uncertainties or dispersions, the proposed generalization of quantum dispersions, and an inconsistency that led us to introduce this generalization. Finally, we outline a quantum theory that encompasses both mechanics and thermodynamics without inconsistencies.

Statistical Thermodynamics

In the interest of brevity, we will present our discussions in the language of quantum mechanics. Though many phenomena encountered in mechanics and thermodynamics can be expressed in terms of classical mechanics, the central point we wish to make cannot.

The dominant view currently held about the physical significance of thermodynamics is based on the interpretation of a "thermodynamic state" as a composite that best describes the knowledge of an observer possessing only partial information about the "actual state" of the system. The "actual state" at any instant of time is defined as a wave function (a pure state or a projection operator) of quantum mechanics. The theories that have recently evolved pursuant to this view have been called informational, though the same concept is the foundation of all statistical thermodynamics.

In such theories the partial or uncertain knowledge of the observer is represented by probabilities, each of which is assigned to one of the possible "actual states." The assignment is achieved by using a postulate or a hypothesis in addition to the laws of mechanics. Recently, the most prevalent postulate is Shannon's criterion. (1, 2, 3, 4) It defines the measure of uncertainty of the observer about the state of the system in terms of the probabilities assigned to the possible "actual states."

The value of the measure just cited ranges from zero to some conditional maximum depending on whether the observer is completely informed or possesses incomplete information about the "actual state" of the system, respectively. Whatever its value, this measure of uncertainty of the knowledge of the observer is identified with the entropy of thermodynamics. Thus, entropy is perceived as an entity characteristic of the knowledge of an observer rather than as an inherent property of matter. In other words, statistical entropy does not have the same physical underpinning as do energy, mass, and momentum.

The interpretation of entropy as a measure of knowledge of an observer cannot be avoided in any of the statistical theories of thermodynamics advanced to date because in all these theories objective reality is represented by pure states only, and such states have no entropy.

Following von Neumann, the "thermodynamic state" is expressed in terms of a statistical matrix or statistical operator that includes combinations of two kinds of probabilities, those that describe the uncertainties characterizing the knowledge of the

observer and that are obtained from the hypothesis added to the laws of mechanics, and those that describe the uncertainties inherent in the nature of matter and that are obtained from the alternative wave functions of the possible "actual states" under consideration. It is a mixed state that consists of a statistical mixture of pure states.

Limited Quantum Uncertainties

In classical mechanics it is assumed that at each instant of time a particle is at a definite position x . Review of experiments, however, reveals that each of many measurements of position of identical particles in identical conditions does not yield the same result. In addition, and more importantly, the result of each measurement is unpredictable. Similar remarks can be made about measurement results of properties, such as energy and momentum, of any system. Close scrutiny of the experimental evidence has ruled out the possibility that the unpredictability of microscopic measurement results are due to either inaccuracies in the prescription of initial conditions or errors in measurement. As a result, it has been concluded that this unpredictability reflects objective characteristics inherent to the nature of matter, and that it can be described only by quantum theory. In this theory, measurement results are predicted probabilistically, namely, with ranges of values and a probability distribution over each range. In contrast to statistics, each set of probabilities of quantum mechanics is associated with a state of matter, including a state of a single particle, and not with a model that describes ignorance or faulty experimentation.

Measurement results and their probabilities can be used to compute the standard deviation or dispersion of the results. If the dispersion in measurements of position x is denoted by Δx , and of momentum p_x along the x -axis by Δp_x , it is found that the product of Δx and Δp_x is greater than a lower limit equal to Planck's constant. This inequality is the well known Heisenberg uncertainty principle. We will see later that other measures of uncertainty or dispersion are possible.

It is customary to represent the probabilities of a quantum-mechanical or "actual" state by a wave function or, equivalently, by a density matrix that is pure or idempotent, i.e., by a matrix that, in diagonal form, has one element equal to unity and all others equal to zero.

Broad Quantum Uncertainties - A Hypothesis

We will hypothesize that quantum conditions exist for which the objective probabilities, inherent to the nature of matter, must be represented by a density matrix that is not idempotent, i.e., a matrix that, in diagonal form, has more than one element different from zero. We will say then that we have objective

uncertainties or dispersions broader than those implied by idempotent density matrices, and we will identify such uncertainties with the thermodynamic state. We will call such matrices mixed.

The hypothesis, and its identification with the thermodynamic state, raises several questions:

- (1) Are broader dispersions consistent with the laws of quantum mechanics?
- (2) Can the statistics represented by a non-idempotent or mixed matrix be reduced to a combination of statistics represented by idempotent or pure matrices?
- (3) Do broader dispersions introduce limitations other than those of conventional quantum theory?
- (4) Are broader dispersions consistent with the second law of thermodynamics?

We elaborate on the answers later in our presentation. Here we wish to emphasize that, if our hypothesis is valid, it has the following consequences:

- (1) The relations between expectation values of properties and the density matrix will be the same as in statistical thermodynamics and, therefore, will conform to the laws of thermodynamics.
- (2) Because we consider one type of uncertainty only, namely the uncertainty inherent to the nature of matter, the laws of thermodynamics must complement the other laws of physics and must apply to all systems (large or small) and to all conditions (nonequilibrium, equilibrium, and stable equilibrium).
- (3) Availability and its related measure entropy become objective properties of matter and cease to represent the extent of knowledge of observers. For example, a single particle has an entropy associated with its state in the same sense that it has energy and momentum associated with that state.
- (4) The breadth of dispersion is measured by entropy, which ranges in value from zero for a pure state (idempotent density matrix) of a given energy, to a maximum for the stable equilibrium (thermodynamic equilibrium) mixed state of the same energy.

An Inconsistency of Statistical Thermodynamics

Our motivation for advancing the hypothesis just cited can be summarized as follows.

Statistical theories of thermodynamics yield many correct and practical results. For example, they yield the canonical and grand canonical distributions for petit and grand systems, respectively; these distributions, which were proposed by Gibbs, have been shown by innumerable comparisons with experiments to describe accurately the properties of quasistable states. Again, they predict the equality of temperatures of systems in mutual stable equilibrium, the Maxwell relations, and the Gibbs equation.

Despite these successes, the premise that the thermodynamic state is a subjective characteristic of a partially informed observer rather than an objective characteristic of matter is questionable because it leads to an inconsistency.

If the thermodynamic state is subjective, then entropy and, therefore, availability are not objective properties of matter. As such, their values can be modified through improved knowledge acquired by means of some measurements. To account for this conclusion without contradicting the requirements imposed by the second law of thermodynamics, Szillard (5), and later on Brillouin (6) and others, advanced the view that acquisition of knowledge requires expenditure of work. Then they showed that increase in availability (or decrease in entropy) is more than offset by the work expended in obtaining better knowledge through measurement.

This view does explain why no work can be obtained out of a system in a stable equilibrium state. However, it does not explain why work can be obtained out of other systems not in stable equilibrium states even by observers totally ignorant about the "actual states" of the systems.

For example, take a collection of identical homogeneous tanks of water, all of which have the same energy, but some of which are isothermal in stable equilibrium states and some, by virtue of gradients in temperature, are not. An observer knowing nothing except the common nature of each tank and the common value of its energy could readily and reproducibly identify those tanks that are not in stable equilibrium states (as opposed to those that are) while expending on the average very much less work than the work that he can extract from them. In other words, it is an experimental fact that every observer can get a net amount of work out of a nonisothermal tank of water without knowing beforehand that it has temperature gradients.

Again, we know from experience that a system in a nonstable state usually, but not necessarily, proceeds towards a stable equilibrium state when isolated. For example, an internally stressed plastic solid may proceed, while isolated, towards an unstressed state at some rate, fast or slow. During such a process, some readily observable characteristics of the system, such as its temperature, change with time. The changes occur in the system rather than in the mind of the observer, or as a result of interventions by the observer. Although the energy of the system has remained unchanged, the maximum value of the energy that can be transferred adiabatically to outside systems has decreased. In other words, the adiabatic availability of the system has changed and there is nothing any observer can do to restore it to its original value short of transferring availability from other systems.

These and other more sophisticated examples have a clear physical implication: departure from stable equilibrium is an inherent characteristic of a system that observers can ascertain reproducibly regardless of their personal knowledge about the

system and, at least for large systems, with negligible work penalty. Otherwise we would not be able to exploit such energy resources as oil wells and uranium deposits.

In thermodynamics, for a given energy a measure of departure from stable equilibrium is the adiabatic availability--the larger the availability, the greater the departure from stable equilibrium. This availability in turn is related to the value of the entropy of the system since the smaller the entropy, the larger the availability. In other words, common sense dictates that entropy is an inherent property of matter in the same sense that energy is an inherent property of matter. Hence, the inconsistency of statistical thermodynamics.

The inconsistency is eliminated by the introduction of the hypothesis of existence of broad quantum dispersions discussed earlier. This hypothesis allows the unification of mechanics and thermodynamics. The unified theory was formally presented in a series of papers (7) in the "Foundations of Physics," and is briefly summarized below.

The Unified Theory

General Remarks. In this section, we will briefly outline an axiomatic theory that encompasses within a single quantum structure both mechanics and thermodynamics. A single quantum structure is necessary because the theory includes quantum mechanics. It is also sufficient because we consider only one type of uncertainty, namely, that inherent in quantum mechanics, and not two types of uncertainty, namely, one for quantum effects and another for incomplete information.

The unification of mechanics and thermodynamics is achieved by adding to three fundamental postulates of quantum mechanics (namely, the correspondence postulate, the mean-value postulate, and the dynamical postulate) two more called the energy and stable-equilibrium postulates, which express the implications of the first and second laws of thermodynamics, respectively.

Because the stable-equilibrium postulate appears to be complementary to, consistent with, and independent of, the postulates of quantum mechanics, the second law emerges as a fundamental law of physics that cannot be derived from the other laws.

In contrast to statistical mechanics, the theory is not concerned with "states" that describe outcomes of measurements performed on an ergodic system over long periods of time, or with "states" that describe the subjective knowledge of an observer possessing only partial information about the "actual state" of a system, or with any other type of "state" that does not correspond to identically prepared replicas of a system as defined later. These distinctions among the various definitions of the term state are motivated by important physical considerations that will be touched upon later.

Several theorems that can be derived from the three postulates of quantum mechanics named above have been presented in the literature. One of these is that to every state of a system specified by means of a given preparation there corresponds a Hermitian operator $\hat{\rho}$, called the density operator, which is an index of measurement statistics. The incorporation of the stable-equilibrium postulate into the theory, however, gives rise to additional theorems that are new to quantum physics. Some of these new theorems are as follows:

1. The maximum energy that can be extracted adiabatically from any system in any state is solely a function of the state. In general, it is smaller than the energy with respect to the ground state, and it can be even zero.
2. For any state of a system, nonequilibrium, equilibrium, or stable equilibrium, a property S exists that is proportional to the total energy of the state minus the maximum energy that can be extracted adiabatically from the system in combination with a reservoir.
3. For statistically independent systems, the property S is extensive, it is invariant during all reversible adiabatic processes, and it increases during all irreversible adiabatic processes.
4. Property S is proportional to $\text{Tr}(\hat{\rho} \ln \hat{\rho})$, where "Tr" denotes the trace of the operator that follows.
5. The necessary and sufficient condition for stable equilibrium is that S should be at its maximum value for fixed expectation values of energy, numbers of particles of species, and external parameters.
6. The only equilibrium states that are stable are those for which the density operator yields the canonical distribution if the system is a petit system, and the grand canonical distribution if the system is a grand system.
7. Property S is defined as the entropy of any state because: (a) for stable equilibrium states, S is shown to be identical to the entropy of classical thermodynamics; and (b) for any state, theorems 2, 3, and 5 above are also theorems of classical thermodynamics.
8. Classical thermodynamics is an exact but special theory resulting from the application of the present unified theory to systems passing through stable equilibrium states. The present theory in general and, therefore, classical thermodynamics in particular apply regardless of whether the system has a small or a large number of degrees of freedom, and regardless of whether the system is small or large in size.

An idea that is believed to be original with the present theory is that the second law, expressed here in the form of the stable equilibrium postulate, implies that systems may be found in mixed states characterized by irreducible uncertainties, i.e., uncertainties that cannot be represented by a mixture of pure states. These uncertainties are associated with the particles or,

more generally, the degrees of freedom of the system. Conversely, the second law is a manifestation of irreducible uncertainties associated with mixed states of a system, and, therefore, with the constituent particles of the system.

The interrelation between irreducible quantal uncertainties and the maximum energy that can be extracted adiabatically from a system represents a radical departure of the present work from other statistical theories, classical or quantum.

In what follows, we present the postulates and some theorems without proofs. Throughout the presentation we assume that the reader is familiar with quantum theory and thermodynamics, and emphasize only points of special relevance to the unified theory.

Postulate 1: Correspondence Postulate. Some linear Hermitian operators on Hilbert space which have complete orthonormal sets of eigenvectors (eigenfunctions) correspond to physical observables of a system. If operator \hat{P} corresponds to observable \bar{P} , then operator $F(\hat{P})$, where F is a function, corresponds to observable $F(\bar{P})$.

Postulate 2: Mean-Value Postulate. To every ensemble of measurements performed on identically prepared replicas of a system there corresponds a real linear functional $m(\hat{P})$ of the Hermitian operators \hat{P} of the system such that if \hat{P} corresponds to an observable property \bar{P} , $m(\hat{P})$ is the arithmetic mean P of the results of the ensemble of \bar{P} -measurements.

Theorem. For each of the mean-value functionals $m(\hat{P})$ there exists a Hermitian operator $\hat{\rho}$ such that for each \hat{P} the following relations hold:

$$P = m(\hat{P}) = \text{Tr}(\hat{\rho}\hat{P}) = \text{Tr}[\rho][P] \quad (1)$$

where "Tr" denotes the trace of the operator or matrix that follows, and "[x]" the matrix of operator \hat{x} . The operator $\hat{\rho}$ is known as the density operator, and $[\rho]$ as the density matrix.

Postulate 3: Energy Postulate. The energy E of a system is defined by the relation

$$E = \text{Tr}(\hat{\rho}\hat{H}) = \text{Tr}[\rho][H]$$

where \hat{H} is the Hamiltonian operator of the system. It is conserved for all processes in an isolated system.

Theorem. For any physically realizable preparation of a separable system subject to fixed parameters and corresponding to density operator $\hat{\rho}$, the probability $W(P_m)$ that a \bar{P} -measurement will yield the eigenvalue P_m of the operator \hat{P} is given by the relation

$$W(P_m) = \text{Tr}(\hat{\rho} \hat{P}_m) = \text{Tr}[\rho][P_m] \quad (2)$$

where \hat{P}_m is the projection operator onto the subspace \hat{P} belonging to eigenvalue P_m .

Theorem. The only possible results of \bar{P} -measurements are the eigenvalues P_m of \hat{P} for all m , where \hat{P} is the operator corresponding to property \bar{P} .

Representation of State. By virtue of its features, the density operator $\hat{\rho}$ is the index of the measurement statistics of quantum physics. It will be seen from Postulate 4 below that $\hat{\rho}$ is also the seat of causality for certain types of changes of state. In addition, it will be shown that, for an ensemble of identically prepared replicas of a system, $\hat{\rho}$ is irreducible; i.e., the ensemble cannot be subdivided into subensembles each of which would yield upon measurement statistics different from the statistics of $\hat{\rho}$. Alternatively, for an ensemble of identically prepared replicas of a system, $\hat{\rho}$ corresponds to irreducible uncertainties of measurement results.

The statements and predictions of our theory apply only to ensembles of identically prepared systems. For such ensembles, the density operator $\hat{\rho}$ may be used to represent the state of the system. This representation gives explicit recognition to the idea that the theory must be confined for the most part to assertions as to the probability that a measurement on a system will yield a particular eigenvalue. Thus, a state will not usually specify the result of each measurement that can be performed on the system in that state.

Postulate 4: Dynamical Postulate.

(1) Any two states of a system that are interconnected by a physical process can always be interconnected by means of one or more reversible processes.

(2) For every system, reversible separable processes always exist for which the temporal development of the density operator $\hat{\rho}$ is given by the relation

$$\hat{\rho}(t_2) = \hat{T}(t_2, t_1) \hat{\rho}(t_1) \hat{T}^+(t_2, t_1) \quad (3)$$

where $\hat{T}(t_2, t_1)$ is a unitary operator in time (the evolution operator), and $\hat{T}^+(t_2, t_1)$ is the Hermitian conjugate of $\hat{T}(t_2, t_1)$.

When the Hamiltonian operator \hat{H} of the system is time independent because the values of the parameters are fixed, then the unitary operator $\hat{T}(t, t_1)$ is given by the relation

$$\hat{T}(t, t_1) = \exp \left[-(2\pi i/h) \hat{H}(t - t_1) \right] \quad (4)$$

whereas, when the Hamiltonian operator $\hat{H}(t)$ is an explicit function of time because the values of the parameters are variable, then $\hat{T}(t, t_1)$ conforms to the relation

$$\partial \hat{T}(t, t_1) / \partial t = -(2\pi i / h) \hat{H}(t) \hat{T}(t, t_1) \quad (5)$$

where h is Planck's constant.

Postulate 5: Stable-Equilibrium Postulate. Any independent separable system subject to fixed parameters has for each set of (expectation) values of energy and numbers of particles of constituent species a unique stable equilibrium state.

This postulate brings into our theory the essence of the second law of thermodynamics. In fact it has been used by Hatsopoulos and Keenan (8) as a form of the second law in the development of classical thermodynamics. Its introduction along with the four other postulates results in a theory that embraces the principles of thermodynamics in addition to those of quantum mechanics with a single physical meaning of the term state.

The stable-equilibrium postulate does not preclude the existence of many equilibrium states for given values of parameters and for given expectation values of energy and numbers of particles. Because any state that satisfies the relation $\hat{\rho} \hat{H} = \hat{H} \hat{\rho}$ could be an equilibrium state, such states are numerous. The postulate asserts, however, that, among the many equilibrium states that can exist for each set of values of parameters, energy, and numbers of particles, one and only one is stable.

This postulate applies to all systems regardless of size or numbers of degrees of freedom, including systems having only one degree of freedom. Of course, the validity of classical thermodynamics for stable equilibrium states of systems with a small number of degrees of freedom was emphasized by Gibbs and others.

It will be shown that the stable-equilibrium postulate restricts application of the theory to states defined by irreducible uncertainties.

Theorem. Starting from a stable equilibrium state, a separable system cannot do work in any adiabatic process involving cyclic changes of parameters (CCP process).

In effect this theorem denies the existence of a perpetual motion machine of the second kind (PMM2), namely, a device acting as a "Maxwellian demon."

Theorem. From any state of a system, the maximum energy that can be extracted adiabatically in a CCP process is the work done in a reversible adiabatic process that ends in a stable equilibrium state. Moreover, the energy change of a system starting from a given state and ending at a stable equilibrium state is the same for all reversible adiabatic CCP processes. We call this energy the adiabatic availability.

Theorem. For any system in any state, a property S exists that remains invariant in any reversible adiabatic process, that increases in any irreversible adiabatic process, and that is

additive for independent separable systems. Moreover, the only expression that satisfies the requirements for S and fits experimental data is

$$S = -k \operatorname{Tr}(\hat{\rho} \ln \hat{\rho}) = -k \operatorname{Tr}[\rho] \ln [\rho] \quad (6)$$

where k is the Boltzmann constant.

Theorem. For any process experienced by an independent separable system having fixed values of energy, numbers of particles, and parameters (namely, a process of an isolated system), the quantity S must either increase or remain invariant.

$$(DS)_{\text{isol}} \geq 0 \quad (7)$$

Relation (7) represents the principle of nondecrease of S .

Graphical Representations

Because a state can be defined by the values of its independent properties, states can be represented by points in a multidimensional property space. In general, the graphical representation is unwieldy because the number of independent properties of a given state can be very large. Nevertheless, useful information often can be summarized by a projection of the multidimensional property space on a two-dimensional plane. One such plane is the $\operatorname{Tr}(\hat{\rho}H)$ vs. $[-k \operatorname{Tr}(\hat{\rho} \ln \hat{\rho})]$ plane, namely the E vs. S plane.

Given a system having fixed numbers of particles (dispersion-free or not) and fixed parameters, the projection of property space on the E - S plane has the shape of the cross-hatched area shown in Figure 1. Each point in this area represents a large number of states having the same values E and S , except for points along the curve $E_g A_0 A_0'$, each of which represents one and only one state.

For the given values of numbers of particles and parameters, and for values of energy greater than the ground-state energy E_g , the boundary $E_g E_1$ at $S = 0$ corresponds to all the pure states of the system, namely, to all states that can be described quantum mechanically by wave functions or idempotent matrices. Thus, pure-state quantum mechanics is zero-entropy physics.

For the given fixed values of numbers of particles and parameters, the curved boundary $E_g A_0 A_0'$ in Figure 1 represents the stable-equilibrium-state relation E vs. S . Its shape is concave as shown because $(\partial E / \partial S)_{n,\beta}$ is an escaping tendency for energy. It reflects the following results of our theory: (a) For each value S_1 for the entropy, stable equilibrium state A_0 is the state of minimum energy; (b) for each value E_1 of energy, stable equilibrium state A_0' is the state of maximum entropy; (c) because each stable equilibrium state is unique, the temperature $(\partial E / \partial S)_{n,\beta}$ is uniquely defined at each point of $E_g A_0 A_0'$; and (d) the ground state

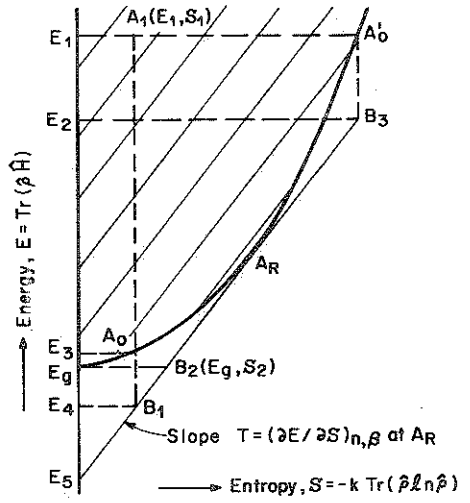


Figure 1. Projection of property space on the energy vs. entropy plane

is nondegenerate and corresponds to $S = 0$ and $T = 0$. The nondegeneracy of the ground state is a consequence of the third law of classical thermodynamics. The boundary $E_g A_0 A_0'$ represents the stable equilibrium states of the system, which may be treated by classical thermodynamics. Thus, stable-equilibrium-state quantum mechanics is constrained-maximum-entropy physics.

Starting from a state on the boundary $E_g A_0 A_0'$ of given energy E_1 , a Maxwellian demon would allow the system to do work only and, therefore, bring it to a state of energy $E_2 < E_1$. But Figure 1 shows that such a process necessarily implies a decrease of entropy, which is impossible.

For a given state A_1 (Figure 1), the energy $E_1 - E_3$ is the adiabatic availability of A_1 . In general, it is seen from the figure that the adiabatic availability varies from $E_1 - E_g$ for a pure state of energy E_1 , to zero for the stable equilibrium state A_0' corresponding to E_1 , depending on the entropy of the state. This limitation on the amount of work that can be extracted from a system with no net change in parameters results from the stable-equilibrium postulate. Although it cannot be derived from the laws of quantum mechanics, it compares favorably with them in scientific validity.

For a given reservoir R at temperature T , a line of slope T can be drawn tangent to $E_g A_0 A_0'$ as shown in Figure 1. The point of tangency A_R is the stable equilibrium state of the system in question that has a temperature $(\partial E / \partial S)_{n, \beta}$ equal to T . For a given state A_1 it can be readily verified that the energy $E_1 - E_4$ is the adiabatic availability of A_1 of the system in combination with reservoir R . It is seen from the figure that this availability varies from a maximum $E_1 - E_5$ for a pure state of energy E_1 , to a minimum $E_1 - E_2$ for the stable equilibrium state A_0' corresponding to E_1 , depending on the entropy of the state. These availabilities of states with values E_1 and $S < S_2$ are greater than the energy $E_1 - E_g$ of the system above the ground state.

Heat interactions are represented in Figure 1 by paths that follow the stable-equilibrium-state curve $E_g A_0 A_0'$. For these interactions, and for these only, the amount dE of energy transferred is uniquely related to the amount dS of entropy transferred, namely, $dE = \delta Q = T dS$. For end states within the cross-hatched area, neither is T definable nor can a unique dS be associated with a given amount of energy transfer dE . It follows that non-adiabatic interactions, in general, are not heat interactions.

In view of these results, entropy can be used as a measure of dispersions. Pure states (idempotent density matrices) have zero entropy, whereas stable equilibrium states have an entropy larger than that of any other state with the same values of energy, parameters, and number of particles.

On the Meaning of State

Here we present the precise definition of a state (pure or mixed) that is subject to the predictions of the unified theory.

The dominant theme of quantum theory is that its causal statements about a system are probabilistic. In other words, the epistemic rule of correspondence, which relates experience to quantum-theoretical states, involves probabilistic concepts in an essential way. In particular, an essential premise of quantum theory is that the physical condition or state of a system at a given time cannot be fully disclosed experimentally unless many measurements are made on replicas of the system prepared in a specified manner. Conversely, an inherent prerequisite of quantum theory is that a preparation of a system be specified and uniquely associated with a state prior to any attempt to reveal experimentally the characteristics of the state. It is this prerequisite that clearly distinguishes quantum mechanics from classical mechanics. It has been discussed extensively in the literature.

The index of measurement statistics corresponding to a given preparation can be expressed in the form of a density operator $\hat{\rho}$. Some preparations result in states described by density operators that are pure (density matrices are idempotent), and some in states described by density operators that are mixed (density matrices are not idempotent). In the context of the quantum mechanical postulates, the preceding sentence is all that need be said about any given preparation and, therefore, any given state.

It is frequently stated that a mixed density operator refers to an ensemble made up of systems each of which is in a pure state. Such a statement, as pointed out by Park (9), is meaningless. In quantum theory, the only experimentally observed reality is that which is revealed by the statistics of measurements performed on an ensemble of identical systems prepared in a specified manner. If a given preparation results in a mixed density operator, then this operator represents the only meaningful reality of the state. Park points out that a general quantum ensemble characterized by a density operator $\hat{\rho}$ can be numerically (as opposed to operationally) subdivided in an infinite variety of ways into pure or mixed subensembles, namely,

$$\hat{\rho} = \sum_k w_k \hat{\rho}_k \quad \text{and} \quad \sum_k w_k = 1 \quad (8)$$

where $\hat{\rho}_k$ is pure or mixed and $0 < w_k < 1$ for all k .

On the other hand, we may raise a different question: Is it possible to establish an operationally meaningful criterion that will distinguish between (a) preparations resulting in dispersions that are due partially to nonquantum effects (or to lack of knowledge) and partially to quantum effects and (b) preparations resulting in dispersions that are solely due to quantum effects? The answer to this question is yes. Prior to presenting the criterion, however, we give an explicit operational definition of the term identically prepared systems.

Definition of Unambiguous Preparation

We shall define a preparation as unambiguous and the resulting ensemble as consisting of identically prepared systems that are in a state $\hat{\rho}$ and that are subject to the predictions of the present unified theory if and only if the subdivision of the ensemble prior to measurement into two or more subensembles, according to any conceivable operational rule, will always result in each subensemble being in the same state $\hat{\rho}$; in other words, the statistics of measurements performed on any subensemble after subdivision will be representable by the same density operator $\hat{\rho}$ as the statistics of the overall ensemble.

For example, consider an ensemble with its members numbered consecutively. Suppose that measurements are made on the subensemble consisting on, say, all even-numbered members, and on the subensemble consisting of all the odd-numbered members. If the probabilities that are derived from the measurements in the first subensemble are identical to the probabilities that are derived from the second subensemble, and this identity obtains for any conceivable subdivision of the original ensemble into subensembles, then the preparation is unambiguous. If measurements performed on the subensembles after subdivision yield statistics that are represented by density operators that are different than that of the overall ensemble, the preparation will be called ambiguous.

These definitions are motivated by the stable-equilibrium postulate, and their importance will become evident from the subsequent discussion.

An Analogy from Probability Theory

The concept of an unambiguous preparation may be illustrated by means of a simple example from probability theory. Suppose that we cut a large number of metallic rods each appearing to have the same length, and that we wish to verify through measurements if indeed the cutting process results in identical lengths. Suppose further, however, that because of either the available measurement technique or some inherent characteristics of the rods, or both, the results of the measurements include a random but statistically unique error so that, even if all the rods were cut to identical lengths, the measurement results would be dispersed. Under these conditions, the question arises: Is it possible to determine whether the rods were prepared by the same cutting procedure?

We may answer this question by proceeding as follows. First, we measure the lengths of the set of all the rods, make a graph of frequency vs. length, and find the average length. Next we divide the rods into two subsets: one consisting of the rods having measured lengths longer than the average, and the other consisting of the rods having lengths shorter than the average. Then we repeat the length measurements and make frequency vs.

length graphs for each subset. Elementary probability theory indicates that, if indeed all the rods were prepared by the same cutting procedure and the observed dispersions were solely due to random effects not associated with the cutting procedure, then the frequency graphs corresponding to the two subsets would be identical. On the other hand, if the rods were not prepared by the same cutting procedure, then the frequency graphs of the two subsets would not be identical.

Theorem - Criterion. Given an ensemble of systems prepared by a preparation Z and consisting of several subensembles, the preparation is unambiguous if: (a) measurements performed from time to time on each system of the ensemble and on each system of the subensembles yield results that are statistically independent; and (b) the joint probabilities for such results are the same for both the ensemble and the collection of the subensembles.

Theorem - Criterion. Given an ensemble of identical systems having a Hamiltonian operator \hat{H} and a density operator $\hat{\rho}$, and consisting of two or more subensembles each of which is prepared by means of an unambiguous preparation, the entropy defined in terms of availability is either equal to $-k \text{Tr}(\hat{\rho} \ln \hat{\rho})$ if the preparations of the subensembles are identical, or smaller than $-k \text{Tr}(\hat{\rho} \ln \hat{\rho})$ if the preparations of the subensembles are different.

On Irreducible Dispersions

The criteria for unambiguous preparations given above provide operational means for distinguishing between dispersions of measurement results that are inherent in the nature of a system and those that are related to voluntary or involuntary incompleteness of experimentation. The former represent characteristics of a system that are beyond the control of an observer. They cannot be reduced by any means, including quantum mechanical measurement, short of processes that result in entropy transfer from the system to the environment. For pure states, these irreducible dispersions are, of course, the essence of Heisenberg's uncertainty principle. For mixed states, they limit the amount of energy that can be extracted adiabatically from the system.

Additional dispersions introduced by voluntary or involuntary incompleteness of experimentation represent inadequacies in the knowledge of observers. As such, though subject to improvement, they are not subject to the full prescriptions of the laws of physics.

The existence of irreducible dispersions associated with mixed states is required by Postulate 5, which expresses the basic implications of the second law of classical thermodynamics. Alternatively, the present work demonstrates that the second law is a manifestation of phenomena characteristic of irreducible quantal dispersions associated with the elementary constituents of matter.

The possibility of a relation between the second law (in the form of the impossibility of a Maxwellian demon) and irreducible dispersions associated with pure states (represented by Heisenberg's uncertainty principle) was suggested by Slater (10). His suggestion was not adopted, however, because Demers (11) proved that dispersions associated with pure states are insufficient to account for the implications of the second law, especially with regard to heavy atoms at low pressures. In the present work, we can relate the second law to quantal dispersions of mixed states because we have accepted the existence of dispersions of mixed states that are irreducible.

In conclusion, in the unified theory the state of any system is described by means of probabilities that are inherent in the nature of the system and that are associated with measurement results obtained from an ensemble of systems of unambiguous preparation. Moreover, the second law of thermodynamics emerges as a fundamental law related to irreducible quantal dispersions of mixed states and applicable to systems of any size, including a single particle.

A key element of the theory is the statement of operational criteria for the distinction between ambiguous and unambiguous preparations (pure or mixed).

For unambiguous preparations, the theory reveals limitations on the amount of work that can be done by a system adiabatically and without net changes in parameters: These limitations are due to irreducible dispersions inherent in the state of the system. They are maximal when the dispersions correspond to a stable equilibrium state.

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