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A Unified Quantum Theory of Mechanics and Thermodynamics. Part I. Postulates

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A unified axiomatic theory that embraces both mechanics and thermodynamics is presented in three parts. It is based on four postulates; three are taken from quantum mechanics, and the fourth is the new disclosure of the existence of quantum states that are stable (Part I). For nonequilibrium and equilibrium states, the theory provides general original results, such as the relation between irreducible density operators and the maximum work that can be extracted adiabatically (Part IIa). For stable equilibrium states, it shows for the first time that the canonical and grand canonical distributions are the only stable distributions (Part IIb). The theory discloses the incompleteness of the equation of motion of quantum mechanics not only for irreversible processes but, more significantly, for reversible processes (Part IIb). It establishes the operational meaning of an irreducible density operator and irreducible dispersions associated with any state, and reveals the relationship between such dispersions and the second law (Part III).

1. INTRODUCTION

The purpose of this paper (Parts I to III) is to present an axiomatic quantum theory which encompasses within a single structure both mechanics and thermodynamics. This purpose is accomplished by adding to three fundamental postulates of quantum mechanics,[2] namely the correspondence postulate, the mean-value postulate, and the dynamical postulate, a fourth

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[2] The axioms of quantum mechanics can be expressed in a number of different ways. In this paper we adopt the axiomatics of Park and Margenau,$^{(1)}$ except for some modifications stated in Section 2.

postulate called the stable-equilibrium postulate, which expresses the basic implications of the second law of thermodynamics.

Because the fourth postulate appears to be complementary to, consistent with, and independent of the first three, the second law of thermodynamics emerges as a fundamental law of physics which is not reflected in the three postulates of quantum mechanics.

In the exposition of the theory a number of terms must be operationally defined so that the theory will have physical meaning. In particular, the terms system, preparation, observable, measurement, and measurement result are used here in accordance with the definitions given by Park.(2) The terms reversible process and adiabatic process are used as in classical thermodynamics.(3) The term state is interpreted as encompassing the most that can be said about the results of all measurements that can be performed on identically prepared replicas of the system. The operational meaning of the expression identically prepared replicas of a system is given a novel definition. Because of its importance to the physical content of the theory, it is discussed in detail in Section 4, Part III.

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 "true state" of a system, or with any other type of "state" that does not correspond to identically prepared replicas of a system as defined in Section 4, Part III. These distinctions among the various definitions of the term state are motivated by important physical considerations which will be discussed in detail in Section 4, Part III.

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.(4) The incorporation of the stable-equilibrium postulate into the theory, however, gives rise to additional theorems which are new to quantum physics and which are derived in Section 3, Parts IIa and IIb. Some of these new theorems are summarized below.

1. The maximum energy that can be extracted adiabatically from any system in any state is solely a function of the state (Theorem 3.7, Part IIa). In general, it is smaller than the energy with respect to the ground state.

2. For any state of a system, nonequilibrium, equilibrium, or stable equilibrium, a property S exists which 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 (Theorem 3.15, Part IIa). The term reservoir denotes a system passing through stable equilibrium states.

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 $\mathrm{Tr}(\hat{\rho} \ln \hat{\rho})$, 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 (Theorem 3.18, Part IIb).

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 (Theorems 3.23 and 3.24, Part IIb).

7. Property S is defined as the entropy of any state corresponding to an unambiguous preparation (Section 4, Part III), because: (a) for stable equilibrium states, S is shown to be identical to the entropy of classical thermodynamics (Section 3.26, Part IIb); and (b) for any state, theorems (2), (3), (5), and (7) 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 dispersions (Section 4, Part III). These dispersions are associated with the particles or, more generally, the degrees of freedom of the system, and limit the energy that can be extracted adiabatically from the system. Conversely, the second law is a manifestation of irreducible dispersions associated with mixed states of a system, and, therefore, with the constituent particles of the system.

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

Finally, it is shown that certain commonly encountered reversible processes in isolated systems cannot be described by the equation of motion of quantum mechanics (Section 3.28, Part IIb). Thus the reversible equation of motion that is part of the dynamical postulate proves inadequate not only for irreversible processes but also for some known reversible processes.

Part I presents the four postulates of the theory. In addition, it includes a relatively large number of explicit definitions of various terms of mechanics and thermodynamics, some of which have been used with different connotations elsewhere. Throughout the paper a general knowledge of quantum mechanical ideas is assumed and only points of special relevance to our theory are emphasized.

2. THE POSTULATES

This section presents some necessary definitions and terminology interspersed with the statements of the four postulates.

2.1. Systems, States, and Properties

We shall use the term *system A* to mean any identifiable collection of degrees of freedom associated with an identifiable collection of matter of zero or nonzero rest mass.

In general, matter that, though not included in A, can influence A we shall call system B. *System A is said to be separable from system B* if and only if the following conditions are satisfied: (1) two Hamiltonian operators $\hat{H}_A$ and $\hat{H}_B$, one for each system, can be identified; (2) each Hamiltonian depends on the generalized coordinates associated with the degrees of freedom of the corresponding system only; and (3) the Hamiltonian of the combined system AB is the sum of the Hamiltonians $\hat{H}_A$ and $\hat{H}_B$.

Influences on a separable system A by systems in its environment will be described by means of *external parameters*(5) or, simply, *parameters* β, which impose limitations on the degrees of freedom of A. Although it represents interactions between A and systems in its environment, an external parameter β can be defined only when its values do not depend explicitly on the variables associated with the degrees of freedom of either A or any system in the environment of A. Examples of parameters are the applied electric field used in the analysis of the Stark effect, and the volume of the container used in the analysis of the energy eigenstates of a gas.

At any instant of time a separable system is in a condition called a *state* which encompasses all that can be said about the results of any measurements or observations that can be performed on identically prepared replicas of the system. The state fixes the values of all the properties of the system. A *property* is any quantity associated with observables whose value is fixed by the state but not by the history of the system. Conversely, a set of independent properties exist which specifies the state. Two properties are called independent if the value of one can be altered without affecting the value of the other. It will be seen that the number of independent properties necessary to specify a state depends on the type of state in question.

By virtue of the quantum mechanical considerations expressed in the postulates that follow, a single measurement of a property performed on a system in a given state does not usually yield a value that is uniquely related to the state. In general, many measurements of the same property, each performed on identically prepared replicas of the system, will yield a variety of values. Each measurement result will be called an *eigenvalue* of the property in question.

In quantum physics, it is not possible to predict from knowledge of the state of the system which eigenvalue a measurement will yield. We may express this fact by saying that it is inherent in nature that either some or all measurements performed on a system in a given state yield results that are *irreducibly dispersed.* Accordingly, the *value of a property* for a given state is defined in terms of the arithmetic average or expectation value of the measurement results.

2.2. Petit and Grand Systems

We shall distinguish two types of separable systems, the petit and the grand. We shall call *petit system* any separable system for which the number of particles and the number of degress of freedom are dispersion-free, namely every measurement yields the same eigenvalues of these two quantities. For example, a collection of a given number of particles which is closed to the transfer of nonzero rest mass and is not subject to creation reactions or annihilation reactions is a petit system.

We shall call *grand system* any separable system for which it is not possible to identify either a dispersion-free number of particles, or a dispersion-free number of degrees of freedom, or both. Systems closed to the transfer of nonzero rest mass but subject to particle-creation and particle-annihilation reactions, such as a photon gas, are examples of grand systems.

2.3. 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* $F(\bar{P})$.

As explained by Park and Margenau (Ref. 1, p. 220), the content of this postulate is slightly different from that of its analogs in typical axiomatics inspired by the work of von Neumann. In its original form, the correspondence postulate included both of the following statements: (1) every Hermitian operator corresponds to a physical observable; and (2) every observable has a Hermitian operator representative. Superselection rules introduced by Wick *et al.*[6] exclude certain Hermitian operators from being observable. By replacing the word *every* in (1) by the word *some*, superselection rules are satisfied. Compatibility of simultaneous measurements introduced by Park and Margenau (Ref. 1, p. 221) excludes certain observables from corresponding to Hermitian operators. In addition, in a unified theory of mechanics and thermodynamics other observables, such as temperature, are excluded from corresponding to Hermitian operators. By replacing the word *every* in (2) by the word *some* the asymmetry between observables and operators is embraced. It is clear that postulate 1 as stated above accommodates both the asymmetry between operators and observables and that between observables and operators.

The rules that specify which operator corresponds to a given observable, such as momentum, energy, etc., of a petit system may be found in any textbook on quantum mechanics and will not be discussed here. Because they are not as widely covered, their extensions to grand systems will be outlined below.

Among the measurements that can be performed on a system is the measurement of the number of its particles. For a petit system such a measurement when repeated will always yield, by definition, the same number. For a grand system, however, such a measurement when repeated can yield a variety of integer values among a set of allowed values consistent with the nature of the system.

In general, a grand system will consist of several species of particles. For each species there will be a corresponding set of allowed eigenvalues for the numbers of particles of the species. For certain grand systems, the set of allowed eigenvalues for the number of particles of a species is assumed to be the set of nonnegative integers. For others, the nature of the system may dictate a more limited range of eigenvalues. Hence, a petit system is a limiting case of a grand system.

By virtue of the rules that apply to petit systems we can associate with each given observable of a grand system several operators, one for each combination of allowed eigenvalues for the number of particles of its species. Each of these operators is in a different Hilbert space denoted by index α and can be regarded as a component of an *overall operator* corresponding to the given observable of the grand system. The overall Hilbert space is the *direct sum* of the mutually orthogonal component Hilbert spaces α. For example, the overall Hamiltonian operator $\hat{H}$, which corresponds to the observable energy of a one-species grand system with possible numbers of particles ranging from one to infinity, will have components $\hat{H}(1)$, $\hat{H}(2),\ldots,$ $\hat{H}(\alpha),\ldots,$ each of the components being the Hamiltonian operator of a petit system having a number of particles $n(1) = 1$, $n(2) = 2,\ldots, n(\alpha) = \alpha,\ldots,$ respectively.

2.4. 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.

Although the statement of postulate 2 is the same as that of postulate 2 of Park and Margenau (Ref. 1, p. 221), its content is different from theirs because of the definition of identical preparation given in detail in Section 4, Part III.

Several elementary quantum theorems derivable from Postulates 1 and 2 will now be stated without proof because the proofs are available in the literature. We assume here that the Hermitian operators have nondegenerate discrete spectra. The extension to spectra that are degenerate, or continuous, or both is straightforward.

2.5. 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⁽⁴⁾:

$$P = m(\hat{P}) = \mathrm{Tr}(\hat{\rho}\hat{P}) \tag{1}$$

The operator $\hat{\rho}$ is known as the *density operator*.

For example, the value E of the energy of a system is given by the relation

$$E = \mathrm{Tr}(\hat{\rho}\hat{H})$$

Again, for a species l having a particle-number operator $\hat{N}_l$, the value n_l of the number of particles is given by the relation

$$n_l = \mathrm{Tr}(\hat{\rho}\hat{N}_l)$$

2.6. Theorem

For any physically realizable preparation of a separable system subject to fixed parameters and corresponding to density operator $\hat{\rho}$, the probability $W(\alpha; P_{\alpha m})$ that a $\bar{P}$-measurement will yield the eigenvalue $P_{\alpha m}$ of the operator $\hat{P}(\alpha)$ in Hilbert space α is given by the relation (Ref. 1, p. 224)

$$W(\alpha; P_{\alpha m}) = \mathrm{Tr}(\hat{\rho}\hat{P}_m(\alpha)) \tag{2}$$

where $\hat{P}_m(\alpha)$ is the projection operator onto the subspace $\hat{P}(\alpha)$ belonging to eigenvalue $P_{\alpha m}$.

2.7. Theorem

The trace of $\hat{\rho}$ is equal to unity (Ref. 1, p. 225) namely

$$\mathrm{Tr}\,\hat{\rho} = 1 \tag{3}$$

2.8. Theorem

The only possible results of $\bar{P}$-measurements are the eigenvalues $P_{\alpha m}$ of $\hat{P}$ for all α and m, where $\hat{P}$ is the operator corresponding to property $\bar{P}$ (Ref. 1, p. 225).

2.9. Theorem

The density operator $\hat{\rho}$ is positive semidefinite (Ref. 1, p. 225).

2.10. Representation of State

By virtue of Theorems 2.5–2.9, the density operator $\hat{\rho}$ is the index of the measurement statistics of quantum physics. It will be seen from Postulate 3 below that $\hat{\rho}$ is also the seat of causality for certain types of changes of state. In addition, it will be shown in Section 4, Part III, that for an ensemble of identically prepared replicas of a system, $\hat{\rho}$ is irreducible, namely that 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 dispersions 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.

In general, for a grand system the numbers of particles of the various species are dispersed and the state yields the probability $W(\alpha; P_{\alpha m})$ that the result of a measurement on the system will be eigenvalues $n_1(\alpha), n_2(\alpha),\dots, n_r(\alpha)$ for the numbers of particles of the species $1, 2,\dots, r$, and eigenvalue $P_{\alpha m}$ of the component $\hat{P}(\alpha)$ of the overall operator $\hat{P}$, for all α and m. The set of numbers $n_1(\alpha), n_2(\alpha),\dots, n_r(\alpha)$ defines Hilbert space α in which $\hat{P}(\alpha)$ can be represented. The density operator $\hat{\rho}$ will have components in some or all of the mutually orthogonal Hilbert spaces α.

For a petit system the numbers of particles of the various species are dispersion-free and the state yields the probability $W(P_m)$ that the result of a measurement of property $\bar{P}$ will be eigenvalue P_m of the operator $\hat{P}$ corresponding to $\bar{P}$, for all m.

2.11. Independent Systems

A separable system A will be called *independent of system B* if and only if all probabilities associated with results of measurements of observables of A are statistically independent of any probabilities associated with B. In other words, independence of A and B implies the absence of correlations between the density operators of A and B.

A system will be called an *independent system* at a given time if at that time it is independent of all systems in its environment.

2.12. Theorem

If A and B are two independent systems in states $\hat{\rho}_A$ and $\hat{\rho}_B$, respectively, the state of the combined system AB is given by the direct product $\hat{\rho}_A \times \hat{\rho}_B$ of $\hat{\rho}_A$ and $\hat{\rho}_B$.

The proof of this theorem follows immediately from the definitions of state, separability, statistical independence, and direct product of operators.

2.13. Certain Thermodynamic Concepts

Prior to stating our third postulate we shall express in quantum mechanical language certain concepts encountered in thermodynamics.

A *change of state* of a separable system A occurs when the eigenvectors of $\hat{\rho}$, or the eigenvalues of $\hat{\rho}$, or the Hilbert space of A, or any combination of these three change. It can be brought about either directly through changes in $\hat{\rho}$ or indirectly by a change in value of at least one of the properties of A, including the parameters, or both. By virtue of Eq. (1) the value of a property can change not only when the density operator $\hat{\rho}$ changes, but also when the property operator $\hat{P}$ changes. If the nature of the system is fixed, a property operator $\hat{P}$ can change if the values of the parameters imposed on the system are altered. For example, for a system with volume as a parameter the Hamiltonian operator $\hat{H}$ changes when the volume is altered.

Changes of state can occur either *spontaneously* while the system is *isolated*, that is, without being affected by or causing any changes in the environment, or as a result of interactions of the system with other systems in its environment. An interaction between two systems A and B is described in terms of the sequence of states of the combined system AB during the interaction, namely the *state path* of AB.

When a system experiences a change of state we shall say that it undergoes a *process*. A *process* is described in terms of the end states of the system and the interactions to which the system is subjected. A process can be defined if and only if the system is separable before and after the interaction because only then can the end states of the system be defined. This definition does not, however, require that the system be separable throughout the process.

If a system is separable throughout a process, its interactions are fully described by the time dependence of its parameters since, by definition, a separable system is affected by its environment only through the values of the parameters. We shall call such processes *separable processes*.

We shall call a process of an isolated system *reversible* if a physically realizable process exists that could restore the system to its initial state with no net changes in the state of the environment. This is the thermodynamic definition of reversibility. It is broader than the definition given in mechanics in terms of the special process of time reversal which can be accomplished only by reversing all momenta.

Any process that does not satisfy the definition of a reversible process we shall call an *irreversible* process.

2.14. Postulate 3: Dynamical Postulate

(a) *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.*

(b) *For every system, reversible separable processes always exist for which the temporal development of the density operator $\hat{\rho}$ is given by the relation* (Ref. 1, p. 224)

$$\hat{\rho}(t_2) = \hat{T}(t_2, t_1)\, \hat{\rho}(t_1)\, \hat{T}^{+}(t_2, t_1) \tag{4}$$

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

$$\hat{T}(t, t_1) = \exp[-(2\pi i/h)\,\hat{H}(t - t_1)] \tag{5}$$

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

$$\partial\hat{T}(t, t_1)/\partial t = -(2\pi i/h)\,\hat{H}(t)\,\hat{T}(t, t_1) \tag{6}$$

where h is Planck's constant.

The range of validity of Postulate 3 differs substantially from that of the dynamical postulates encountered in axiomatic treatments of quantum mechanics, including the treatment of Park and Margenau (Ref. 1, p. 224). The conventional form of the dynamical postulate, that is essentially Eq. (4) regarded as universally applicable, is not adequate for a unified theory of mechanics and thermodynamics for two basic reasons. First, as shown in Section 3.28, Part IIb, certain reversible separable processes of importance to thermodynamics cannot be described by Eq. (4) because their end states are not related by a unitary operator. Second, whereas thermodynamics does not exclude the existence of irreversible processes, Eq. (4) describes reversible processes only.

Of course, Eq. (4) may also not apply to a process for which the system is not separable throughout the process. For a nonseparable system A undergoing a reversible process with system B, however, Eq. (4) may apply to the combined system AB provided that the end states for AB are related by a unitary operator.

2.15. Unitary Processes

If the density operators corresponding to the initial and final states of a process are related by a unitary operator, it will be called a *unitary process.* It follows from the dynamical postulate that a reversible separable process can always be found that connects the end states of a unitary process.

2.16. Theorem

Given a separable system in a state $\hat{\rho}$, the value of any property that is invariant during all unitary processes for both fixed and time-dependent parameters, that is additive for independent systems, that is an arithmetic mean of measurement results, and that is not explicitly dependent on the numbers of particles of constituent species is of the form

$$I = c \operatorname{Tr}(\hat{\rho} \ln \hat{\rho}) \tag{7}$$

where c is a fixed constant.

The proof of this important theorem is given in Appendix A, and its physical significance will be discussed in Section 3.15, Part IIa.

2.17. Classification of States

We shall call a state for which the value of at least one property of a system changes with time a *nonsteady state*. For such a state, the density operator $\hat{\rho}$ is an explicit function of time. We shall use the term *steady state* to designate any state for which the values of all the properties of a system are time invariant. By virtue of Eq. (1), the sufficient condition for a system to be in steady state is that both the density operator $\hat{\rho}$ and all the property operators $\hat{P}$ be time invariant.

A special kind of steady state is a steady state of an isolated system. It will be called an *equilibrium state*. For an isolated system the operators corresponding to various properties, including the Hamiltonian, will be time invariant, and therefore time invariance of $\hat{\rho}$ is both necessary and sufficient for the system to be in an equilibrium state. If the temporal development of $\hat{\rho}$ follows Eq. (4), the necessary and sufficient condition for $\hat{\rho}$ to be an equilibrium state is that $\hat{\rho}$ and $\hat{T}$ commute and therefore that $\hat{\rho}$ and $\hat{H}$ [Eq. (5)] commute, namely

$$\hat{\rho}\hat{H} = \hat{H}\hat{\rho} \tag{8}$$

Equation (8) will be satisfied if and only if the eigenvectors of $\hat{\rho}$ are eigenvectors of $\hat{H}$, namely the energy eigenvectors. In other words, the necessary and sufficient condition for equilibrium is that the density matrix $[\rho]$ be diagonal in the energy representation. All states, steady or nonsteady, that are not equilibrium are called *nonequilibrium states*.

Equation (8) is neither necessary nor sufficient for equilibrium if the system undergoes a process that is not described by Eq. (4). A state for which $\hat{\rho}$ obeys Eq. (8), whether it is an equilibrium state or not, will be called a *stationary state*.

An equilibrium state of an isolated system may always be made to change by means of interactions if the isolation of the system is interrupted.

Interactions that cause the change of the state of a system from an equilibrium state to some other state may not leave net effects in the environment. If they leave no net effects in the environment, we shall say that while the state of the system changed, the process in the environment was a *cyclic process* or a *cycle.*

If it is possible to alter an equilibrium state and leave no net effects in the environment, we shall say that the initial equilibrium state is *not stable.* Accordingly, we shall define a *stable equilibrium state* as that equilibrium state that will *always* be restored if the state of the environment undergoes a cycle.

From the definitions just cited, it follows that: (1) Steady states constitute the most general category of time-invariant states; (2) a stationary state is a special case of a steady state; (3) an equilibrium state is a special case of a stationary state; and (4) a stable equilibrium state is a special case of an equilibrium state.

Apart from their time dependence, states can be classified into two types, *pure* and *mixed.* A state $\hat{\rho}$ is pure if and only if $\hat{\rho} = \hat{P}_\psi$, where $\hat{P}_\psi$ is the projection operator onto the span of Hilbert vector $\psi\rangle$ (Ref. 4, pp. 321–323). By virtue of Eq. (3) it follows that all eigenvalues of the density operator of a pure state are equal to zero except for one which is equal to unity.

The definition of pure states implies the following theorems$^{(7)}$: (1) A necessary and sufficient condition for a state to be pure is that its density matrix be idempotent; (2) a pure state can be fully described by means of a vector in Hilbert space; it is the eigenvector of $\hat{\rho}$ corresponding to the eigenvalue that is equal to unity; (3) for a pure state that is an eigenstate of an operator corresponding to a property the value of that property is dispersion-free; and (4) for pure states only, Eq. (4) is entirely equivalent to the time-dependent Schrödinger equation.

A pure state can be an equilibrium or a nonequilibrium state. It is an equilibrium state (stationary state) only if it is described by a vector that is an eigenvector of $\hat{H}$. It will be shown later that among all the pure equilibrium states of a system, only the ground state, namely the state of lowest energy, is a stable equilibrium state. All other stable equilibrium states with energies greater than that of the ground state are, therefore, mixed states.

2.18. Theorem

If a system is in any pure state other than the ground state, its energy may always be decreased by means of a unitary process that corresponds to zero net changes of the values of the parameters of the system.

Proof: For given values of parameters, any pure state is related to the ground state (state of lowest energy) by a unitary operator. By virtue of Postulate 3b, it follows that a unitary process corresponding to zero net changes of the values of the parameters can be found to connect any pure state to the ground state and, therefore, to a state of lower energy in accordance with Theorem 2.18. This theorem has also been shown by von Neumann (Ref. 4, Chapter V) to be a theorem of the conventional form of the dynamical postulate.

2.19. Postulate 4: 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 (Ref. 3, p. 367) as a form of the second law in the development of classical thermodynamics. Its introduction along with the three postulates of quantum mechanics 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 which satisfies Eq. (8) 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 himself as well as Wilson.(8)

It will be shown in Part III that the stable-equilibrium postulate restricts application of the theory to states defined by irreducible dispersions. Irreducible dispersions are defined in Section 4, Part III.

This completes the presentation of the four postulates of the present unified theory. A number of important theorems that can be deduced from these postulates are discussed in Part II.

APPENDIX A: PROOF OF THEOREM 2.16

We shall seek a property with a value I that is invariant in all unitary processes, that is additive for independent separable systems, that is an arithmetic mean of measurement results, and that is not explicitly dependent on the numbers of particles of constituent species.

Given a separable system A in state A_1, let the density operator $\hat{\rho}$ have complete sets of eigenvalues $\{y_k\}$ and orthonormal eigenvectors $\{v_k\}$ that are finite. By virtue of Eq. (4), except for the numbers of particles, the only invariants in all unitary processes are the eigenvalues of $\hat{\rho}$. Consequently, the value I of a property that remains invariant in these processes must be solely a function of all eigenvalues $y_1, y_2, \ldots, y_k, \ldots$, and, since it is an arithmetic mean, it must be of the form (Theorem 2.5)

$$I = \sum_m y_m i_m(y_1, y_2, \ldots) \tag{A.1}$$

where $i_m(y_1, y_2, \ldots)$ is the mth diagonal element of the matrix associated with the operator of the property in the v-representation.

By means of a unitary process α_{12} involving cyclic changes in parameters, state A_1 can be connected to state A_2 which has the same eigenvalues $y_1, y_2, \ldots, y_k, \ldots$ but arbitrarily rearranged eigenvectors $v_1, v_2, \ldots, v_k, \ldots$, with respect to the ordering of the eigenvalues $y_1, y_2, \ldots, y_k, \ldots$. Conversely, process α_{12} can be regarded as resulting in an arbitrary rearrangement of the eigenvalues $y_1, y_2, \ldots, y_k, \ldots$, with respect to a fixed ordering of the eigenvectors $v_1, v_2, \ldots, v_k, \ldots$. Since it is invariant in all α_{12}, the quantity I must be a symmetric function of the eigenvalues $y_1, y_2, \ldots, y_k, \ldots$ of the form

$$I = \sum_m y_m i(y_m) = \sum_m f(y_m) \tag{A.2}$$

where $i(y)$ and $f(y)$ are functions of y only.

Given two independent separable systems A and B in states A_1 and B_1, respectively, let the eigenvalues of the density operator for A_1 be $y_1, y_2, \ldots, y_m, \ldots, y_M$, and those for B_1 be $z_1, z_2, \ldots, z_n, \ldots, z_N$. If I is an additive property, then I_{AB} for the combined system AB must be the sum of I_A and I_B, namely

$$I_{AB} = \sum_m^M \sum_n^N f(y_m z_n) = \sum_m^M f(y_m) + \sum_n^N f(z_n) \tag{A.3}$$

For $y_k = 1$ and $y_m = 0$ for $m \neq k$, and $z_l = 1$ and $z_n = 0$ for $n \neq l$, Eq. (A.3) yields

$$-f(1) + (M \times N - M - N) f(0) = 0 \tag{A.4}$$

Because the number M of eigenstates of system A is independent of the number N of eigenstates of system B, it follows from Eq. (A.4) that

$$f(0) = 0 \qquad \text{and} \qquad f(1) = 0 \tag{A.5}$$

Keeping all y_m and z_n fixed except for y_k and y_l which we vary so that

$$dy_k + dy_l = 0 \qquad \text{for arbitrary } k \text{ and } l \tag{A.6}$$

we find that Eq. (A.3) yields

$$\sum_n z_n \frac{df(y_k z_n)}{d(y_k z_n)} - \frac{df(y_k)}{dy_k} = \sum_n z_n \frac{df(y_l z_n)}{d(y_l z_n)} - \frac{df(y_l)}{dy_l} \tag{A.7}$$

Since y_k and y_l are arbitrary, each side of Eq. (A.7) must be at most a function of all the z_n only, so that upon differentiating with respect to y_k we obtain the relation

$$\sum_n z_n^2 \frac{d^2f(y_k z_n)}{d(y_k z_n)^2} - \frac{d^2f(y_k)}{dy_k^2} = 0 \tag{A.8}$$

Moreover, keeping all z_n fixed except for z_r and z_s which we vary so that

$$dz_r + dz_s = 0 \qquad \text{for arbitrary } r \text{ and } s \tag{A.9}$$

we find that Eq. (A.8) yields

$$2z_r \frac{d^2f(y_k z_r)}{d(y_k z_r)^2} + z_r^2 y_k \frac{d^3f(y_k z_r)}{d(y_k z_r)^3} = 2z_s \frac{d^2f(y_k z_s)}{d(y_k z_s)^2} + z_s^2 y_k \frac{d^3f(y_k z_s)}{d(y_k z_s)^3} \tag{A.10}$$

or, equivalently,

$$2x \frac{d^2f(x)}{dx^2} + x^2 \frac{d^3f}{dx^3} = c \tag{A.11}$$

where c is a fixed constant. The solution of Eq. (A.11) subject to conditions (A.5) is given by the relation

$$f(x) = cx \ln x \tag{A.12}$$

and, consequently,

$$I = \sum_m f(y_m) = c \sum_m y_m \ln y_m = c \operatorname{Tr}(\hat{\rho} \ln \hat{\rho}) \tag{A.13}$$

Equation (A.13) is valid also for states $\hat{\rho}$ having an infinite number of eigenvalues $y_1, y_2, ..., y_k, ...$. The proof of this statement, however, will not be given here.

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