A Unified Quantum Theory of Mechanics and Thermodynamics. Part IIb. Stable Equilibrium States[1]

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Part IIb presents some of the most important theorems for stable equilibrium states that can be deduced from the four postulates of the unified theory presented in Part I. It is shown for the first time that the canonical and grand canonical distributions are the only distributions that are stable. Moreover, it is shown that reversible adiabatic processes exist which cannot be described by the dynamical equation of quantum mechanics. A number of conditions are discussed that must be satisfied by the general equation of motion which is yet to be discovered.

3. THEOREMS RELATED TO THE STABLE-EQUILIBRIUM POSTULATE (CONTINUED)

This part of the paper continues the presentation of theorems related to the stable-equilibrium postulate with special emphasis on stable equilibrium states, and presents certain commonly encountered reversible processes that cannot be described by the equation of motion of quantum mechanics (Postulate 3, Part I).

3.17. Theorem

A state A_0 of a system is a stable equilibrium state if and only if the value S_0 for A_0 is larger than that of any other state of the system having the same values of energy, numbers of particles, and parameters as A_0.

Proof: For fixed values of energy, numbers of particles, and parameters, let us assume that state A_0 of maximum S is not a stable equilibrium state. From the definition of a stable equilibrium state (Section 2.17, Part I) it follows that a process can be found beginning with state A_0 and ending with a different state A_1 for which the environment undergoes a cycle. Since initially S is at a maximum, the final state A_1 would have a value S_1 smaller than that of the initial state A_0. This result, because it violates Theorem 3.15, Part IIa, is absurd. We conclude that a state of maximum S as specified above is a stable equilibrium state.

For fixed values of energy, numbers of particles, and parameters it is shown in Sections 3.23 and 3.24 that the expression for S [Eq. (25), Part IIa] results in a unique maximum corresponding to a unique state. According to the conclusion just cited, this unique state must be a stable equilibrium state. Moreover, it must be the only stable equilibrium state. If it were not, more than one stable equilibrium state would correspond to the given values of energy, numbers of particles, and parameters, contrary to the stable-equilibrium postulate.

3.18. Theorem

For given values of energy, numbers of particles, and parameters the value of S for the stable equilibrium state must be the maximum value.

This theorem is a restatement of Theorem 3.17 and constitutes a *criterion for stable equilibrium*.

3.19. Theorem

Given a system in a stable equilibrium state corresponding to (expectation) values E for energy, n_1, n_2,..., n_r for the numbers of particles of the r species, and β_1, β_2,..., β_s for the values of the s parameters, the (expectation) value P of any property $\bar{P}$ is fully and uniquely determined by the given values E, n_1, n_2,..., n_r, β_1, β_2,..., β_s.

The proof of this theorem follows immediately from the definition of state and the uniqueness of the stable equilibrium state (stable-equilibrium postulate).

3.20. Theorem

For stable equilibrium states of a system the value P of any property is a single-valued function of the form

$$P = P(E, n_1, n_2,..., n_r, \beta_1, \beta_2,..., \beta_s). \qquad (27)$$

This theorem is a restatement of Theorem 3.19. It is known in classical thermodynamics as the *state principle*.[13] It applies to stable equilibrium states only.

In general, a large number of values of independent properties is required for the specification of a state, nonequilibrium or equilibrium. The set of such values has been called a *quorum*.[14] For a stable equilibrium state, however, the stable-equilibrium postulate requires that the number of properties in a quorum be at a minimum. This minimum is the result of the nature of the stable equilibrium state and not of the observer's coarse specification, inadequate knowledge, or inability to carry out complicated numerical calculations.

Several relations of the form of Eq. (27) for various properties can be combined to express the value of any property as a function of any desirable set of independent properties of stable equilibrium states. We shall call relations between such values of properties *equations of stable equilibrium states.*

Two equations of stable equilibrium states that are basic to subsequent discussion are the relations

$$S = S(E, n_1, n_2, ..., n_r, \beta_1, \beta_2, ..., \beta_s) \tag{28}$$

and

$$E = E(S, n_1, n_2, ..., n_r, \beta_1, \beta_2, ..., \beta_s) \tag{29}$$

3.21. Theorem

For two systems A and B with continuous and differentiable functions (28) and (29), each having fixed parameters, each being in a stable equilibrium state, and each being capable of exchanging only energy with the other, the necessary and sufficient condition for mutual stable equilibrium is that the partial derivative of the energy [Eq. (29)] with respect to S be the same in both systems. In symbols,

$$\left(\frac{\partial E}{\partial S} \right)_{n,\beta}^A = \left(\frac{\partial E}{\partial S} \right)_{n,\beta}^B \tag{30}$$

where the superscript denotes the system and the subscripts the quantities that are kept fixed during the differentiation. The partial derivative $(\partial E/\partial S)_{n,\beta}$ for a system in a stable equilibrium state will be denoted by T, i.e.,

$$T = (\partial E/\partial S)_{n,\beta} \tag{31}$$

The proof of this theorem follows immediately from the criterion for stable equilibrium (Theorem 3.18) applied to combined system AB (Ref. 15, p. 398).

By virtue of the principle of nondecrease of S (Theorem 3.16, Part IIa) it can be shown that T represents an "escaping tendency" for energy, namely when $(\partial E/\partial S)^A_{n,\beta} > (\partial E/\partial S)^B_{n,\beta}$ then energy can flow spontaneously from A into B.

The quantity T can be uniquely defined only if a system in a stable equilibrium state can be identified, because then and only then is E a unique function of $S, n_1, n_2, ..., n_r, \beta_1, \beta_2, ..., \beta_s$.

3.22. Theorem

For two systems A and B with continuous and differentiable functions (28) and (29), each having fixed parameters, each being in a stable equilibrium state, and each being capable of exchanging both energy and particles with nonzero rest mass of species i, for $i = 1, 2, ..., r$, with the other, the necessary and sufficient conditions for mutual stable equilibrium are that the partial derivatives $(\partial E/\partial S)_{n,\beta}$ and $(\partial E/\partial n_i)_{S,n,\beta}$ be the same in both systems, where E is given by Eq. (29). In symbols

$$\left(\frac{\partial E}{\partial S}\right)^A_{n,\beta} = \left(\frac{\partial E}{\partial S}\right)^B_{n,\beta}$$

$$\left(\frac{\partial E}{\partial n_i}\right)^A_{S,n,\beta} = \left(\frac{\partial E}{\partial n_i}\right)^B_{S,n,\beta} \qquad \text{for} \quad i = 1, 2, ..., r$$

(32)

The partial derivative $(\partial E/\partial n_i)_{S,n,\beta}$ for a system in a stable equilibrium state will be denoted by μ_i, i.e.,

$$\mu_i = (\partial E/\partial n_i)_{S,n,\beta} \qquad \text{for} \quad i = 1, 2, ..., r \tag{33}$$

The proof of this theorem follows immediately from the criterion for stable equilibrium (Theorem 3.18) applied to combined system AB. Each property μ_i, like property T, can be uniquely defined only if a system in a stable equilibrium state can be identified, because then and only then is E a unique function of $S, n_1, n_2, ..., n_r, \beta_1, \beta_2, ..., \beta_s$. Each μ_i can be shown to represent an "escaping tendency" for species i.

3.23. Theorem

A petit system (Section 2.2, Part I) is in a stable equilibrium state $\hat{\rho}_0$ if and only if the eigenvectors of $\hat{\rho}_0$ are the energy eigenvectors of the system and the eigenvalues $x_i{}^0$ of $\hat{\rho}_0$ are related to the energy eigenvalues ϵ_i of the system by the relation

$$x_i{}^0 = \frac{\exp(-\epsilon_i/kT)}{Q_c} \qquad \text{for} \quad i = 1, 2, ... \tag{34}$$

where $T = (\partial E/\partial S)_{n,\beta}$, and

$$Q_c = \sum_i \exp(-\epsilon_i/kT) = \text{Tr} \exp(-\hat{H}/kT) \tag{35}$$

The quantity Q_c is called the *canonical partition function*. For petit systems, $\hat{\rho}_0$ will be called the *canonical operator*, and the set $x_1{}^0, x_2{}^0, ..., x_i{}^0, ...$ the *canonical distribution*.

The proof of the theorem follows from the criterion for stable equilibrium, namely the maximization of S [Eq. (25), Part IIa, for $c = -k$], subject to the requirements

$$E = \text{Tr}(\hat{\rho}\hat{H}) = \text{const} \qquad \text{and} \qquad \text{Tr}\,\hat{\rho} = 1$$

Consistent with the stable-equilibrium postulate, the state [Eq. (34)] for which S is maximum at fixed values of energy and of parameters is unique.

Substituting Eq. (34) into the expression for S [Eq. (25), Part IIa, for $c = -k$], we find the following equation of stable equilibrium states:

$$S = (E/T) + k \ln Q_c \tag{36}$$

3.24. Theorem

A grand system (Section 2.2, Part I) with operators that have components in many Hilbert spaces α (Section 2.10, Part I) is in a stable equilibrium state $\hat{\rho}_0$ if and only if the eigenvectors of $\hat{\rho}_0$ are the energy eigenvectors of the system and the eigenvalues $x_{\alpha i}^0$ of $\hat{\rho}_0$ are related to the energy eigenvalues $\epsilon_{\alpha i}$ of the system by the relation

$$x_{\alpha i}^0 = \frac{\exp\{-[\epsilon_{\alpha i} - \sum_l^r \mu_l n_l(a)]/kT\}}{Q_g} \qquad \text{for all } \alpha \text{ and } i \tag{37}$$

where the index α denotes the component Hilbert spaces, the index i the various energy eigenvalues within each Hilbert space,

$$T = (\partial E/\partial S)_{n,\beta}, \qquad \mu_l = (\partial E/\partial n_l)_{S,n,\beta}$$

$$Q_g = \sum_\alpha \sum_i \exp\left[-\frac{\epsilon_{\alpha i} - \sum_l^r \mu_l n_l(\alpha)}{kT}\right] \tag{38}$$

$$= \text{Tr} \exp\left(-\frac{\hat{H} - \sum_l^r \mu_l \hat{N}_l}{kT}\right)$$

and $\hat{N}_l$ is the particle-number operator for species l. The quantity Q_g is called the *grand canonical partition function*. For grand systems, $\hat{\rho}_0$ will be called the *grand canonical operator*, and the set $x_{11}^0, x_{21}^0, ..., x_{i\alpha}^0, ...$ the *grand canonical distribution*.

The proof of the theorem follows from the criterion for stable equilibrium as for Theorem 3.23 except that here the requirements are that $E = \text{Tr}(\hat{\rho}\hat{H}) = \text{const}$, $n_l = \text{Tr}(\hat{\rho}\hat{N}_l) = \text{const}$ for each l, and $\text{Tr } \hat{\rho} = 1$.

Substituting Eq. (37) into the expression for S, we find the following equation of stable equilibrium states:

$$S = \frac{E}{T} + \frac{\sum_i^r \mu_i n_i}{T} + k \ln Q_g \tag{39}$$

3.25. Theorem

For a petit system in a state A_1 with a density operator $\hat{\rho}_1$, the available energy, namely the maximum work W_{max}^R that can be obtained from the system in combination with a reservoir R for which $(\partial E/\partial S)_{n,\beta}^R = T_0$, is given by the relation

$$W_{\text{max}}^R = \text{Tr}[\hat{\rho}_1(\hat{H} + kT_0 \ln \hat{\rho}_1)] + kT_0 \ln \text{Tr}[\exp(-\hat{H}/kT_0)] \tag{40}$$

Proof: By virtue of Theorem 3.13, Part IIa, the available energy is given by the work done in a reversible adiabatic process in the combined system AR in which system A starts from state A_1 and ends in a state A_0 in mutual stable equilibrium with reservoir R and with no net changes in parameters. In this process the quantity S for the combined system AR is invariant and, therefore, the value S_0 for state A_0 is given by the relations

$$\begin{aligned} S_0 &= S_1 - DS_R \\ &= -k \, \text{Tr}(\hat{\rho}_1 \ln \hat{\rho}_1) - DS_R \end{aligned} \tag{41}$$

where DS_R is the change of the quantity S_R of the reservoir. Moreover, by virtue of Theorem 3.22 and Eqs. (35), (36), and (41) the energy E_0 of state A_0 and the change in energy DE_R of reservoir R are given by the relations

$$\begin{aligned} E_0 &= T_0 S_0 - kT_0 \ln Q_c \\ &= -kT_0 \, \text{Tr}(\hat{\rho}_1 \ln \hat{\rho}_1) - kT_0 \ln \text{Tr}[\exp(-\hat{H}/kT_0)] - T_0 DS_R \end{aligned} \tag{42}$$

and

$$DE_R = T_0 DS_R \tag{43}$$

Finally, the energy E_1 of state A_1 is given by the relation

$$E_1 = \text{Tr}(\hat{\rho}_1\hat{H}) \tag{44}$$

Subtracting Eqs. (42) and (43) from Eq. (44), we get Eq. (40).

If the initial state is an energy eigenstate having an eigenvalue ϵ_j, Eq. (40) reduces to

$$W_{\max}^R = \epsilon_j + kT_0 \ln \text{Tr}[\exp(-\hat{H}/kT_0)]$$

$$= \epsilon_j - \epsilon_1 + kT_0 \ln \left\{1 + \sum_{i \neq 1} \exp[(\epsilon_i - \epsilon_1)/kT_0]\right\}$$

(45)

Equation (45) is a simple example showing that the available energy can exceed the energy $\epsilon_j - \epsilon_1$ of the system with respect to the ground-state energy ϵ_1.

An expression similar to Eq. (40) can be readily derived for grand systems.

3.26. Identification of Certain Properties with Properties Encountered in Classical Thermodynamics

For a system passing through stable equilibrium states, the energy can be expressed in the form of Eq. (29). By virtue of Eqs. (31) and (33), the differential dE can be expressed in the form

$$dE = T\,dS + \sum_i^r \mu_i\,dn_i + \sum_i^s \left(\frac{\partial E}{\partial \beta_i}\right)_{S,n,\beta} d\beta_i \tag{46}$$

For a reversible adiabatic process passing through stable equilibrium states for fixed n_i, the first and second terms of the right-hand member vanish. Moreover, the energy $(dE)_{\text{rev}}^a$ becomes the negative $-\delta W$ of the work done in the process. It follows that

$$(dE)_{\text{rev}}^a = \sum_i^s \left(\frac{\partial E}{\partial \beta_i}\right)_{S,n,\beta} d\beta_i = -\delta W \tag{47}$$

The symbol δ is used because work is not a property of a system and δW therefore is not a perfect differential.

In general for a reversible process passing through stable equilibrium states for fixed n_i, Eqs. (46) and (47) yield

$$T\,dS = (dE + \delta W)_{\text{rev}} \tag{48}$$

In classical thermodynamics, the nonwork part of the energy transferred to the system, namely $[dE - (-\delta W)]_{\text{rev}}$, in this reversible process is called *heat* and is denoted by δQ. It follows from Eq. (48) that

$$\delta Q = T\,dS \tag{49}$$

and from Eqs. (46) and (49) that heat is an interaction that alters the energy of a system having fixed values of parameters β and numbers of particles n_i as it passes through stable equilibrium states. The heat δQ is not a perfect differential because Q is not a property of a system.

It is seen from Eq. (49) that $\delta Q/T$ is a perfect differential for any reversible process passing through stable equilibrium states for fixed β and n_i. In classical thermodynamics, T is called temperature. The integral $\int (\delta Q/T)$ evaluated between some reference stable equilibrium state and a second stable equilibrium state is called the entropy of the second state. Upon comparing theoretical and experimental values of entropy for a simple system passing through stable equilibrium states, such as a perfect gas, the fixed constant c in Eq. (25), Part IIa, is identified as being $-k$, the negative of the Boltzmann constant.

We have already shown (Part IIa) that: (1) For any system in any state, nonequilibrium, equilibrium, or stable equilibrium, S is invariant in all reversible adiabatic processes; and (2) for any system in any state, S is nondecreasing in all adiabatic processes in general. Since these two features are characteristic of the entropy of stable equilibrium states of classical thermodynamics, from here on we shall call S the *entropy of the system* irrespective of whether the state is stable equilibrium or not.

Comparing Eq. (46) with the generalized Gibbs equation (Ref. 15, p. 470) for stable equilibrium states in classical thermodynamics, we conclude that μ_i is the *total potential of species i, for* all i.

3.27. 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 $\mathrm{Tr}(\hat{\rho}\hat{H})$ vs. $[-k\, \mathrm{Tr}(\hat{\rho}\ln \hat{\rho})]$ 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 approximately the shape of the cross-hatched area shown in Fig. 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
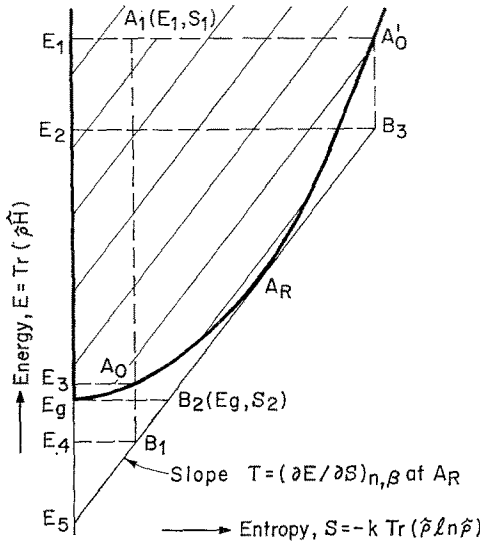
Fig. 1. Projection of property space on the energy
vs. entropy plane.

states that can be described quantum mechanically by projection operators. 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 Fig. 1 represents the stable equilibrium state relation E vs. S (Theorem 3.20). Its shape is concave as shown because $(\partial E/\partial S)_{n,\beta}$ is an escaping tendency (Theorem 3.21). It reflects the following results of our theory: (1) For each value S_1 for the entropy, stable equilibrium state A_0 is the state of minimum energy (Theorem 3.3, Part IIa); (2) for each value E_1 of energy, stable equilibrium state A_0' is the state of maximum entropy (Theorem 3.18); (3) 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 (4) the ground state 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 and, therefore, bring it to a state of energy $E_2 < E_1$. Figure 1 shows that such a process necessarily implies a decrease of entropy, which, according to Theorem 3.16, Part IIa, is impossible.

For a given state A_1 (Fig. 1), the energy $E_1 - E_3$ is the adiabatic availability Ψ_1 of A_1 (Theorem 3.7, Part IIa). 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 Fig. 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 available energy Ω_1 of A_1 of the system in combination with reservoir R [Eq. (40)]. It is seen from the figure that the available energy 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. The available energies of all 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. Finally, it is seen from the figure that, in general, the available energy is greater than the adiabatic availability (Theorem 3.11, Part IIa).

For a state A_1, no adiabatic process involving no net changes in numbers of particles can end in states to the left of the line $A_1 A_0$ (Fig. 1) because such a process would result in work (decrease in E) in excess of the decrease in available energy (Theorem 3.13, Part IIa).

Heat interactions are represented in Fig. 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 nonadiabatic interactions, in general, are not heat interactions.

3.28. On Nonunitary, Reversible, Separable Processes

The conventional interpretation of the dynamical postulate includes explicitly or implicitly the statement that all processes of a separable system or of a separable combination of interacting systems are unitary (reversible, separable). In a unified theory of mechanics and thermodynamics this statement is not valid because, as will be shown below, nonunitary, reversible separable processes must exist and irreversible, separable processes probably exist.
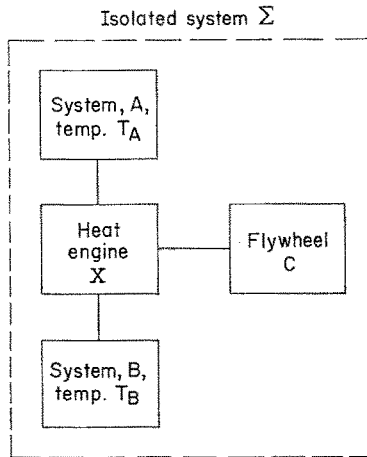
Isolated system Σ

Fig. 2. Schematic of a commonly encountered nonunitary, reversible, separable process.

A process commonly encountered in thermodynamics is that involving the transfer of energy (heat) from a system A in a stable equilibrium state at temperature T_A to a system B in a stable equilibrium state at a lower temperature T_B for fixed values of parameters of both A and B. Such a process is made reversible by interposing between A and B a reversible cyclic device X, called a heat engine, that does work. The work done by X can be used to increase the energy of a fourth system C, such as a frictionless flywheel, by means of a unitary process for C (Fig. 2).

The process for the combined system Σ consisting of A, B, X, and C is separable because Σ can be isolated from the environment. It is also reversible because all systems participating in the process can be restored to their initial states, by running the cycle of X in the reverse direction, leaving no net effects on the environment of Σ (Section 2.13, Part I).

For a given energy change ΔE_A of A, we will consider a reversible process for Σ in which the work done on C is given by the Carnot expression [Appendix G, Eq. (G. 6)]. In thermodynamics, this process is corroborated by many experiments. We shall call it the *Carnot process*.

It is shown in Appendix G that, during the reversible Carnot process, A and B pass through stable equilibrium states and remain statistically independent (uncorrelated) because, for a given ΔE_A, if either the process is irreversible or A and B do not pass through stable equilibrium states, or A and B are correlated, the work done on C is less than that of the Carnot process [Eq. (G. 6)].

Moreover, it is shown in Appendix G that for many systems Σ the Carnot process is not unitary.

A second example of a nonunitary, reversible, separable process is the reversible, adiabatic process of an isolated combined system AC in which A starts from a mixed, nonstable state A_1 and does work on C untill all its adiabatic availability is transferred to C (Theorem 3.7, Part IIa)—namely until system A reaches a stable equilibrium state for which the entropy is the same as at A_1. The density operator for the final state is canonical, whereas for the initial nonstable state A_1 it is not. Because the eigenvalues of these two density operators differ, they cannot be connected by a unitary operator. System C, on the other hand, can be a work element (Appendix C, Part IIa) that undergoes a unitary process. It follows that the combined system AC undergoes a nonunitary, reversible, separable process.

Finally, a third example of a nonunitary, reversible, separable process is the reversible, separable process of a system A starting from a pure state A_1 and doing work in combination with reservoir R until all its available energy (Theorem 3.11, Part IIa) is transferred to a work element C undergoing a unitary process—namely until system A reaches a state in mutual stable equilibrium with the reservoir. The eigenvalues of the density operator of the initial state of the combined system AR consist of an infinite number of zeros plus the canonically distributed eigenvalues of the reservoir (Section 2.17 and Theorem 2.12, Part I, and Theorem 3.23). The eigenvalues of the density operator of the final state of AR are canonically distributed and are all different from zero (Theorem 3.23). It follows that ARC undergoes a nonunitary, reversible, separable process.

3.29. On Irreversible Processes

In this section we shall discuss the following three questions: (1) Does Postulate 4 or any other correct statement of the second law of thermodynamics demand the existence of irreversible processes? (2) What is the experimental evidence that supports the existence of irreversible processes? (3) What are some of the possible causes of irreversibility?

The stable-equilibrium postulate neither precludes nor demands the existence of irreversible processes; in other words, no basic arguments of the present theory are critically dependent on the existence of irreversibility. Indeed this conclusion is true for several well-known statements of the second law of classical thermodynamics, including that of Carathéodory.[16] It is a commonly encountered fallacy, however, that the second law and, therefore, classical thermodynamics are based on the existence of irreversibility. Except for a few inequalities, classical thermodynamics and all its implications about physical systems would be equally valid and

nontrivial in the physics of a reversible universe as in that of an irreversible one.

For example, for a reversible universe Postulate 4 would still imply the existence of stable equilibrium states. Without irreversibility a system in a nonstable state can reach a stable equilibrium state only as a result of interactions with other systems in the environment that involve transfer of entropy to the system or work done by the system, or both.

Ample experimental evidence exists that isolated systems starting from nonstable states spontaneously attain stable equilibrium states without transfer of energy from or to the environment. Such processes could be explained by postulating the existence either of irreversible processes or of reversible processes that involve transfer of entropy but not energy from the environment.

Because perfect isolation may be difficult to achieve in practice, an explanation often cited for irreversibility is that weak and complicated interactions from the environment force a system to approach a stable equilibrium state. But this explanation avoids, rather than solves, the problem. Weak and complicated interactions between a system and its environment could cause an increase of the entropy of a system without appreciably affecting its energy. Such interactions, however, would have effects on the environment. Two cases can be distinguished: (1) The entropy of the system increases by the same amount that the entropy of the environment decreases. This process involves no irreversibility. (2) The entropy of the system increases but the entropy of the environment does not decrease by a corresponding amount. Here the irreversibility occurs in the environment. We are left with the problem of explaining why interactions that cause flow of entropy into a system do not decrease the entropy of the environment.

In conclusion, we can recognize three possibilities, each of which requires further clarification: (1) The universe is reversible and its total entropy remains invariant while being redistributed among various systems. (2) Part of the universe is irreversible and part is reversible. Entropy is generated in the irreversible part and transferred to the other part. (3) Irreversible processes exist for all parts of the universe. Each of these possibilities would be governed by an equation of motion which is yet to be discovered.

3.30. On the General Equation of Motion

Equation (4) is incomplete because it describe neither reversible, nonunitary processes nor irreversible processes. A general equation of motion that describes all known processes has yet to be discovered. All we can say about such an equation of motion is the following: (1) It must describe nonunitary processes in general and, in the limit of unitary processes, it must

reduce to Eq. (4), Part I; (2) for an irreversible process in an isolated system it must result in a decrease with time of the quantity $Tr(\hat{\rho} \ln \hat{\rho})$; and (3) for all processes in an isolated system it must imply the invariance of the quantity $Tr(\hat{\rho}\hat{H})$. The first two requirements result from the four postulates of the present unified theory. The third is a result of the first law of classical thermodynamics (Ref. 15, p. 22).

For completeness, some form of the first law of classical thermodynamics should have been added to the four postulates of our theory. Although for unitary processes it is not needed because the dynamical postulate implies the conservation of $Tr(\hat{\rho}\hat{H})$, for other processes the first law is necessary until the general equation of motion is found. It was omitted to avoid diversion of attention from more important aspects of the theory.

This completes the presentation of a number of important theorems of the present unified theory. As already stated, the theory applies only to states that are defined by irreducible dispersions. Irreducible dispersions are discussed in Part III.

APPENDIX G. PROOF OF NONUNITARITY OF PROCESS SHOWN IN FIG. 2

For systems A and B in Fig. 2, which are initially independent, and for a given decrease ΔE_A of energy of A, we will consider the Carnot process that does maximum work on flywheel C.

By virtue of Theorem 3.13, Part IIa, we know that the process must be reversible. It follows that during this process the entropy of Σ is invariant. Moreover, because X and C undergo a cyclic and unitary process, respectively, their entropies are invariant and, therefore, the entropy of AB is invariant.

Let the initial and final states of AB, A, and B be $\hat{\rho}_0^{AB}$, $\hat{\rho}_0{}^A$, and $\hat{\rho}_0{}^B$ ($\hat{\rho}_0^{AB} = \hat{\rho}_0{}^A \times \hat{\rho}_0{}^B$) and $\hat{\rho}^{AB}$, $\hat{\rho}^A = \mathrm{Tr}_B \hat{\rho}^{AB}$, and $\hat{\rho}^B = \mathrm{Tr}_A \hat{\rho}^{AB}$, respectively, where Tr_X denotes partial tracing over the Hilbert space of system X. Because AB undergoes a reversible process, its initial and final entropies satisfy the relation

$$S(\hat{\rho}_0^{AB}) = S(\hat{\rho}^{AB}) \tag{G.1}$$

where

$$S(\hat{\rho}_0^{AB}) = S(\hat{\rho}_0{}^A) + S(\hat{\rho}_0{}^B) \tag{G.2}$$

but

$$S(\hat{\rho}^{AB}) \leqslant -k \, \mathrm{Tr}(\hat{\rho}^A \ln \hat{\rho}^A) - k \, \mathrm{Tr}(\hat{\rho}^B \ln \hat{\rho}^B) \tag{G.3}$$

In relation (G.3), the equality holds if and only if A and B are independent, namely $\hat{\rho}^{AB} = \hat{\rho}^A \times \hat{\rho}^B$, and entropies can be indentified for A and B,
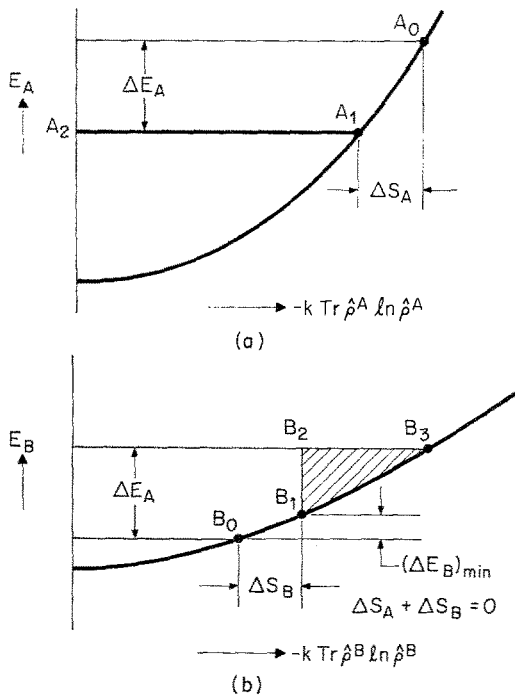
Fig. 3. E vs. $-k \operatorname{Tr}(\rho \ln \rho)$ diagrams for systems in
Fig. 2: (a) system A, (b) system B.

because statistical correlations result always in the entropy of AB being smaller than the sum $-k \operatorname{Tr}(\hat{\rho}^A \ln \hat{\rho}^A) - k \operatorname{Tr}(\hat{\rho}^B \ln \hat{\rho}^B)$. In the presence of correlations, no entropies can be defined for A and B, and the sum $-k \operatorname{Tr} \hat{\rho}^A \ln \hat{\rho}^A - k \operatorname{Tr}(\hat{\rho}^B \ln \hat{\rho}^B)$ does not represent the entropy of AB.

The states of A and B can be shown schematically on E vs. $-k \operatorname{Tr}(\hat{\rho} \ln \hat{\rho})$ diagrams (Fig. 3). For a given decrease ΔE_A, the possible final states $\hat{\rho}^A$ must be on line $A_1 A_2$ (Fig. 3a). We see from the figure that stable equilibrium state A_1 corresponds to the minimum decrease ΔS_A of $-k \operatorname{Tr}(\hat{\rho}^A \ln \hat{\rho}^A)$.

By virtue of the law of conservation of energy and relations (G.1)–(G.3), the possible final states $\hat{\rho}^B$ must be in the cross-hatched area $B_1 B_2 B_3$ (Fig. 3b), where line $B_1 B_2$ is determined by the minimum possible ΔS_A transfer to B, and line $B_2 B_3$ by the maximum possible energy transfer ΔE_A to B. We see from the figure that stable equilibrium state B_1 corresponds to minimum increases $\Delta S_B (\Delta S_A + \Delta S_B = 0)$ and ΔE_B and, therefore, to maximum work W_C done on $C [W_C = -\Delta E_A - (\Delta E_B)_{min}]$. Moreover, since for states A_1 and B_1

$$\Delta S_A + \Delta S_B = 0 \qquad\qquad \text{(G.4)}$$

it follows from Eq. (G.1) that

$$S(\hat{\rho}^{AB}) = -k \, \mathrm{Tr}(\hat{\rho}^A \ln \hat{\rho}^A) - k \, \mathrm{Tr}(\hat{\rho}^B \ln \hat{\rho}^B)$$
$$= S(\hat{\rho}^A) + S(\hat{\rho}^B) \tag{G.5}$$

namely that the final stable equilibrium states A_1 and B_1 of the Carnot process are independent ($\hat{\rho}^{AB} = \hat{\rho}^A \times \hat{\rho}^B$).

It can be readily shown that the work W_C done during the Carnot process is given by the relation

$$W_C = -\Delta E_A - (\Delta E_B)_{\min} = -\int_0^{\Delta E_A} \frac{T_A(E_A) - T_B(E_B)}{T_A(E_A)} \, dE_A \tag{G.6}$$

where $T(E)$ denotes the temperature vs. energy relation of each system, and E_B depends on E_A because of the condition of reversibility.

Next, let the eigenvalues of the canonical operators $\hat{\rho}_0^A$ and $\hat{\rho}_0^B$ for the initial states be $x_1^0, x_2^0,..., x_i^0,...$ and $y_1^0, y_2^0,..., y_j^0,...$; and let the eigenvalues for the states $\hat{\rho}^A$ and $\hat{\rho}^B$ at the end of an infinitesimal Carnot process be $x_1^0 + dx_1, x_2^0 + dx_2,..., x_i^0 + dx_i,...$ and $y_1^0 + dy_1, y_2^0 + dy_2,..., y_j^0 + dy_j,...$, respectively; here

$$\sum_i dx_i = 0 \qquad \text{and} \qquad \sum_j dy_j = 0 \tag{G.7}$$

Contrary to the conclusion stated in Section 3.28, let the Carnot process for any combined system Σ in Fig. 2 be unitary. Because systems X and C undergo unitary processes, it follows that the combined system AB must also undergo a unitary process and, therefore, that the density operators for the final and initial states of A and B must satisfy the relation

$$\mathrm{Tr}(\hat{\rho}^A \times \hat{\rho}^B)^n = \mathrm{Tr}(\hat{\rho}_0^A \times \hat{\rho}_0^B)^n \qquad \text{for} \quad n = 2, 3,... \tag{G.8}$$

Differentiating Eq. (G.8), we find that the eigenvalues of the density operators must satisfy the relations

$$\sum_j (y_j^0)^n \sum_i (x_i^0)^{n-1} dx_i + \sum_i (x_i^0)^n \sum_j (y_j^0)^{n-1} dy_j = 0 \qquad \text{for} \quad n = 2, 3,... \tag{G.9}$$

Using the differential relations

$$dx_i = d \frac{\exp(-\epsilon_i^A/kT_A)}{\sum_i \exp(-\epsilon_i^A/kT_A)} = \frac{x_i^0}{kT_A^2} [\epsilon_i^A - E_A(T_A)] \, dT_A \tag{G.10}$$

and

$$dy_j = d \frac{\exp(-\epsilon_j^B/kT_B)}{\sum_j \exp(-\epsilon_j^B/kT_B)} = \frac{y_j^0}{kT_B^2} [\epsilon_j^B - E_B(T_B)] \, dT_B \tag{G.11}$$

and substituting into Eq. (G.9), we find in due course

$$\frac{dT_A}{dT_B} = -\frac{T_A^2}{T_B^2}\frac{E_B(T_B) - [\sum_j (y_j^0)^n \, \epsilon_j^B/\sum_j (y_j^0)^n]}{E_A(T_A) - [\sum_i (x_i^0)^n \, \epsilon_i^A/\sum_i (x_i^0)^n]}$$

$$= -\frac{T_A^2}{T_B^2}\frac{E_B(T_B) - E_B(T_B/n)}{E_A(T_A) - E_A(T_A/n)} \quad \text{for} \quad n = 2, 3,\dots \quad (G.12)$$

where ϵ_i^A and ϵ_j^B and T_A and T_B denote the energy eigenvalues and the temperatures of the initial states of A and B, and $E_A(T)$ and $E_B(T)$ the energies of A and B at temperature T, respectively. Equation (G.12) is valid if and only if its right-hand side is independent of the value of n. This requirement is satisfied if and only if

$$E_A(T) \propto T^a \quad \text{and} \quad E_B(T) \propto T^a$$

namely if and only if the energies $E_A(T)$ and $E_B(T)$ depend on the same power a of T. Since the energy of all systems in stable equilibrium states does not depend on the same power of T, it follows that, in general, the Carnot process of Σ is not unitary, and the conclusion stated in Section 3.28 is valid. For example, if A is a perfect gas and B has T-dependent specific heats, then E_A is proportional to T but E_B is not proportional to T, and Eq. (G.12) is not valid for all values of n.

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