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PAUL M. QUAY

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The Statistical Thermodynamics of Equilibrium*

LASZLO TISZA† AND PAUL M. QUAY‡

Department of Physics and Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts

A statistical thermodynamics is developed in terms of extensive variables (additive invariants) distributed over a cellular division in space. In general, this distribution is governed by randomness and by correlations. The present theory, however, deals explicitly only with randomness, although correlations are implicit in the so-called fixed variables of the system. Because of this restriction, the theory is valid only for the fluctuations of coupled systems that have reached their equilibrium; hence we call it the statistical thermodynamics of equilibrium, briefly STE. A set of postulates is advanced, the essence of which is the requirement that distribution functions (d.f.) exist for two basic coupling situations. It is implicit that the system has a memory-loss mechanism; and the d.f. does not depend on past history (ergodic property). Such qualitative assumptions are sufficient to derive the Gibbsian d.f.'s in their quantitative form. These d.f.'s describe the coupling of finite systems with infinite environments and can be used to analyze typical situations of measurement by the methods of mathematical statistics. The present point of view sheds some new light on the ergodic problem and on the role of Nernst's law in completing the definition of thermodynamic equilibrium. An attempt is made to clarify the relations between entropy, information, and uncertainty by advancing a generic notion, the dispersal of a d.f., that subsumes these concepts as special cases.

INTRODUCTION

In 1910, Einstein developed a theory of fluctuations by introducing statistical concepts into thermodynamics and without making any explicit reference to the

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† Currently on leave of absence at the Laboratoire de Chimie Physique de la Faculté des Sciences de Paris. John Simon Guggenheim Memorial Fellow.

‡ National Science Foundation Fellow, Massachusetts Institute of Technology, 1956–58. *Present address:* Department of Physics, Case Institute of Technology, Cleveland, Ohio.

coordinates of the particles constituting the system (*1*). His point of departure was the inversion of Boltzmann's relation $S = k \log W$ connecting entropy and probability (*2*). Instead of reducing the entropy to probabilities defined in microscopic terms (or, rather, to numbers of microstates), Einstein obtained the relative probabilities of fluctuation states in terms of differences of entropy. He went beyond the Boltzmann theory, inasmuch as he could consider general thermodynamic systems rather than only assemblies of weakly interacting particles. Moreover, he avoided the difficulties connected with the equipartition law without explicitly invoking the quantum theory. Of course, as a counterpart to these improvements, Einstein's theory renounced much of the space-time description that is implicit in Boltzmann's theory and did not provide the framework for the calculation of the thermodynamic functions from molecular parameters.

Einstein's work was independent of Gibbs' statistical mechanics, which had appeared a few years earlier (*3*) and which constitutes the other major generalization of Boltzmann's theory. Both of the generalized theories account for the fluctuations of thermodynamic quantities in systems in equilibrium with their environment. Gibbs' theory is conceptually the more satisfactory, but the quantitative discrepancies between the theories vanish asymptotically for large (macroscopic) systems and the two formalisms are used in the literature interchangeably. The two theories differ considerably, however, in their approach to the foundations. In contrast to Einstein's thermodynamic attitude, Gibbs attempted to derive the statistical theory of equilibrium ensembles from classical mechanics.

The approach taken by the present paper can be considered as a synthesis of selected aspects of those of Einstein and Gibbs. We shall follow the former in choosing a thermodynamic, rather than mechanical point of departure, but we shall sharpen the argument to arrive at a derivation of the more elaborate Gibbsian statistical formalism. This means, of course, that we detach Gibbs' ensemble theory from its connections with classical mechanics.

It is apparent that Gibbs' theory consists of a statistical and of a mechanical part which are only loosely connected with each other. The first aspect of this connection is the simple and important statement that the mechanical phase space provides the so-called sample space for the probability distribution function (d.f.) of the statistical theory. A quantum-mechanical version of this result is incorporated into the present theory, and thus contact is established with the standard calculations of quantum statistics. A second and more deeply reaching aspect of the connection is the derivation of the d.f.'s from purely mechanical principles, handled by Gibbs only through the verbal arguments of the famous Chapter XII. The traditional approach to the foundations required that this loose connection should be tightened. Although the numerous attempts to carry out this program led to interesting developments, there is a consensus of opinion that the problem has not been solved.

In view of this situation, several ideas have been recently offered to put the theory of ensembles on a statistical rather than on a mechanical foundation. Thus, Mandelbrot showed how important parts of statistical thermodynamics can be subsumed under standard procedures of mathematical statistics, without any reference to micromechanics (*4*). Moreover, Jaynes and others have proposed the concepts of information and statistical uncertainty as the sole organizing principles for statistical thermodynamics (*5*). Probability and entropy are interpreted in a purely subjective sense and are supposed to reflect our knowledge of the system only in the sense of information theory (*5a*).

The present paper has certain elements in common with these latter contributions, but departs from them in others. Granted the importance of recognizing the mathematical formalism that is suitable for a physical discipline, it is desirable that the latter should be structured around physical organizing principles. Such an organizing principle is provided by thermodynamics itself if its scope is extended by the introduction of statistical elements of a physical nature (*6*). This is a break with the traditional notion that this discipline is to be strictly macroscopic. If, however, thermodynamics is considered as a theory of measurement, it is fitting for it to catch up with the extension of experimentation into the microscopic domain.

The shortcoming of classical thermodynamics is its lack of space-time detail. This paper is part of a program in which such detail is injected into the theory in successive stages. The theory here developed is called STE, which is short for statistical thermodynamics of equilibrium.[1] This paper was preceded by another (*7*), in which the macroscopic thermodynamics of equilibrium or, briefly, MTE has been developed. We shall refer to (*7*) as (*MTE*).

The relation between MTE and STE is very close, and is explained in terms of their postulational bases in Section I. Both theories deal with the distribution of additive invariants over disjoint regions of space. In MTE, one considers only the equilibrium values of these invariants, collectively denoted by X, as determined from a phenomenological extremum principle. In the deeper theory, STE, the X's are considered as random variables whose averages are the equilibrium values of MTE.

The central problem confronting statistical theories is the interplay of randomness with correlations stemming, say, from a dynamical law. The simplest statistical theory, STE, deals only with pure randomness. This formal specification leads in a natural way to the Gibbsian theory of equilibrium ensembles.

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[1] We adhere to the convention of using capitalized abbreviations to denote theories with an explicitly formulated postulational basis. Terms such as "thermostatics" or "thermodynamics" are used in a looser, more conventional sense.

The derivation given in Section II utilizes a fundamental work of Szilard (*8*) which, after some adjustments, fits harmoniously into the present context.[2] An extension to several random variables is found in Section III. Although these results are formally identical to those well known in statistical mechanics, there is a considerable difference in their scope and conceptual interpretation. Some of these questions are discussed in the remainder of the paper. Section IV contains the elements of a theory of measurements based on the concept of parameter estimation (see ref. *4*). This approach yields a reinterpretation of thermodynamic formalism which is applicable even to very small isolated systems. Section V deals with asymptotic theories in which the number of degrees of freedom is allowed to tend to infinity. In Section VI, we discuss the role of the ergodic property in STE and the relation of entropy and information.

The discussion of the approach to equilibrium (H-theorem) is outside the scope of STE since such a discussion requires an explicit handling of correlations. Thus, our approach implies a subdivision of the foundation problem that is quite similar to the one suggested by Schafroth (*9*).

I. DEFINITIONS AND POSTULATES

The postulational basis of STE consists of two parts. That which is summarized in Section I,A is held in common with MTE, and for a fuller discussion we refer to Section I,A of (MTE). Section I,B contains the statistical postulates that replace the entropy-maximum postulate of MTE.

A. Definitions and Postulates from MTE

The independent variables of both MTE and STE are additive, conserved quantities, briefly additive invariants, $X_1, X_2, \cdots$. We shall usually interpret these variables as: internal energy U, mole numbers of chemical components $N_1, N_2, \cdots$, and volume V.[3]

A thermodynamic simple system is a region in space for which particular

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[2] Szilard's results were neither developed in nor integrated with the main current of statistical physics. Indeed, his method appears rather *ad hoc* in that context. Recently, however, Mandelbrot showed (*4*) that the method can be considered as an application of the concept of "sufficiency" developed in mathematical statistics. Although we believe that the use of such techniques in statistical thermodynamics is well worth exploring (cf. Section IV), our adaptation of Szilard's method is self-contained and does not rely on specialized statistical knowledge.

[3] This interpretation raises questions of validity: are these variables indeed additive and invariant? Thus, the energy is not exactly additive. Moreover, the identification of the chemical components of the system, hidden innocuously beneath the subscripts of the N's, is not absolute. The identifying properties themselves can vary, depending on the presence or absence of catalysts or anticatalysts, which act, in this way, as constraints on the molecular level. For a further discussion, we refer to pp. 21, 22 of (*MTE*).

values X' of the additive invariants are specified within some short interval of time. Disjoint simple systems can be built up into composite systems or, conversely, we may divide a system into subsystems, sometimes referred to as cells.

Thermodynamic *processes* may be of various sorts, but what we consider primarily is the passage of some quantity X from one system to another. The systems are separated by *walls* that are *restrictive* of the passage of some of the quantities, say X_λ, and nonrestrictive of all the others denoted by X_j. Such a wall is symbolized by $W[X_j]$ on the assumption that the full set of X's has been given. The restrictions on a system imposed by its walls are referred to as *constraints.*

We consider now the set of all variables X', X'', $\cdots$ associated with the various subsystems. By choosing appropriate linear combinations, it is possible to classify these into *free* and *fixed* variables: the former are free to change while the latter are held constant by the existing constraints. We shall distinguish these types of variables by Roman and Greek subscripts respectively. The distinction between free and fixed variables X_k and X_λ is fundamental for STE, and the details of physical interpretation seem sometimes only secondary. Thus, there is a far-reaching analogy between processes of energy and mass transfer; nevertheless, the differences between such processes are by no means negligible. The universal role of the energy manifests itself thermodynamically in the fact that one can realize in practice a transfer of energy without a transfer of any other X, a true one-variable process, whereas if any of these other X's are transferred, the process is accompanied by a transfer also of energy and we have a process described by at least two variables.

We shall emphasize the close connection of our results with quantum mechanics, particularly with the fact that the energy may have a mixed discrete-continuous spectrum. However, we shall ignore those subtler effects for whose description the density matrix is essential. Accordingly we assume the following postulates in addition to those listed in I, A (MTE):

P a5. The values of the variables X are precisely measurable except, possibly, for an arbitrary constant.

Also connected with quantum mechanics is the following postulate through which the concept of the ground-state of a system is introduced.

P a6. For simple systems contained in a finite volume, the range of variation of the X's has a lower bound. In particular, the lowest energy of a system is a function of its fixed variables. In a context in which the latter are held constant, the lowest energy can be set equal to zero.

We shall not discuss in this paper the thermodynamic processes involving *work*, the discussion of which in STE adds little to the results available already in MTE. To be sure, the concept of work gives rise to significant statistical problems (*10*); but the discussion of these involves the "memory" or "persistence" of the previously realized states and belongs to a more subtle theory that deals with the interplay of randomness and correlations.

B. Definitions and Postulates on Statistical Equilibrium

We develop now the statistical concept of equilibrium characteristic of STE. As we have seen, the coupling of thermodynamic systems is effected by the exchange of additive invariants. We now postulate that this exchange be governed by statistical laws, the properties of which are expressed in merely *qualitative* postulates *P b1–4*. Together with those of Section A, these postulates suffice for the derivation of the *quantitative* laws of thermodynamic equilibrium, the effects of fluctuations included. These postulates taken together, then, implicitly define thermodynamic equilibrium. Contrary to what one might expect from a superficially critical analysis, this procedure is not circular because its conclusions are subject to a very exacting experimental verification, as we shall see in Section IV,D.

D b1. Similar systems [symbol $(x_k \mid x_\lambda)$]: A set of systems describable in terms of the same selection of variables X, and such that each fixed quantity X_λ has the same value x_λ in each system, while the values of the free variables X_k take on random values x_k in the various systems. We denote a particular, instantaneous value of a variable X by x.[4]

At least one of the X's has to be fixed, or else the system would be undefined. We shall usually consider the volume as a fixed variable; often also, the total mass, for one-component systems, preferably expressed in terms of the mole numbers.

D b2. Ensemble [symbol $e(x_k \mid x_\lambda)$, or $e(x_\lambda)$]: An unlimited set of similar systems.

Two different interpretations of this abstract definition are useful. In the first, the similar systems are distinct and independent replicas of some particular system, all subject to the same constraints as this latter. In the second, called a *temporal ensemble*, the similar systems represent simply the results of measurements on the free variables of a single system at discrete instants of time t_n $(n = 1, 2, \cdots)$.

A quantitative description of the values of the free variables can be given only in terms of statistical distribution functions (d.f.) the nature of which depends on the type of physical situation considered, and exhibits, in general, an interplay of randomness with correlations arising as a consequence of molecular dynamics.

The physical situation considered in STE is thermodynamic equilibrium.

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[4] Throughout this paper we shall use the vertical bar to separate free and fixed variables in the symbols of ensembles and in expressions of probability. Since the specification of the system includes the proper selection of the set of all the variables X, strictly speaking, similar systems should be designated as $(x_k \mid X, x_\lambda)$.

The corresponding statistical theory is that of independent random variables. This means that correlation effects do not explicitly affect the statistical distribution of the free variables, although molecular correlations are in various ways implicit in the theory, in particular, in the selection of the fixed variables which determine the chemical identity of the system. While in (MTE) we assumed that the fixed variables determine the asymptotic equilibrium values of the free variables, we now make the weaker assumption that the fixed variables enter into the specification only of the d.f. of the free variables. In STE, then, equilibrium is characterized by the existence of a unique d.f., which we shall postulate in two typical situations: first, for the equilibrium of one finite system with another; and second, for the equilibrium of a finite system with an infinite environment called a reservoir.

P b1. Statistical equilibrium: Finite systems. Consider an ensemble $e(x_\lambda', x_\lambda'')$ of isolated systems, each of which is composed of a subsystem (x_λ') in contact with a subsystem (x_λ'') through a wall $W[X_k]$. For each member of e, let $(x_k \leqq X_k < x_k + dx_k)$. After a sufficiently long time ("aging"), the ensemble e is said to be in equilibrium with respect to the distribution of the X_k, and is then decomposed into $e'(x_\lambda')$ and $e''(x_\lambda'')$. The probability that, under these conditions, a member of e' should possess values of the X' less than x' is given by a unique conditional (cumulative) d.f.

$$\begin{aligned}\mathfrak{F}(x_k' \mid x_k ; x_\lambda', x_\lambda'') &\equiv \mathfrak{F}(x_k' \mid x_k) \\ &= \Pr\{X_k' < x_k' \mid x_k \leqq X_k < x_k + dx_k ; x_\lambda', x_\lambda''\}\end{aligned} \tag{1.1}$$

where Pr means "probability" and $x_k = x_k' + x_k''$.

In spite of its qualitative character, this postulate is very strong, since it states that $\mathfrak{F}$ is uniquely determined by the conditioning parameters to the right of the vertical bar in the argument. In order to appreciate the meaning of this requirement, we have to list some of the factors that *could* be relevant for the determining of the d.f. but actually are not. First, $\mathfrak{F}$ is determined by the present values of the fixed variables and does not depend on their past history. Thus there is implicitly assumed the existence of a memory-loss mechanism within systems approaching equilibrium.

Secondly, either of the interpretations of an ensemble given in *D b2* may be used; so far as $\mathfrak{F}$ is concerned, they are wholly equivalent. This equivalence of the two modes of ensemble-representation of a system is known as the *ergodic property*. We shall discuss this point in more detail in Section VI.

We shall also use the differential d.f.

$$d\mathfrak{F}(x_k' \mid x_k) = \mathfrak{F}(x_k' + dx_k' \mid x_k) - \mathfrak{F}(x_k' \mid x_k). \tag{1.2}$$

For continuous distributions one has

$$d\mathfrak{F}(x_k' \mid x_k) = \mathfrak{f}(x_k' \mid x_k)\, dx_k', \tag{1.3}$$

where $\mathfrak{f}$ is a probability density. For discrete nonsingular distributions:

$$d\mathfrak{F}(x_k' \mid x_k) = \mathfrak{f}(x'_{kn} \mid x_k) = \mathfrak{f}_n(x_k' \mid x_k), \tag{1.4}$$

where n is an integer and the intervals of the X_k' have been chosen small enough so that $\mathfrak{f}_n$ is the probability of a single "level." The distribution function, $d\mathfrak{F}$, as also the corresponding ensemble. is referred to as *microcanonical*.

In *P b1* the systems (x_λ') and (x_λ'') are on an equal footing. We now let the size of (x_λ'') tend to infinity. In this case *P b1* no longer ensures the existence of a d.f. for the X_k'; and if such a distribution exists, it is not conditioned by $x_k' + x_k''$, since this is infinite.

Although at first sight the transition to infinite systems or reservoirs seems to lead to difficulties, in reality this limiting process brings about important simplifications. There are many reservoirs that are equivalent to each other as environments of finite systems although they differ considerably in their intrinsic structure. Granted the possibility that the detailed structure of the reservoir has an effect on an individual observation of the state of a coupled finite system, still this effect is averaged out over the ensemble, and this is our only concern in the present theory. The precise definition of the equivalence of reservoirs constitutes the first element in a generalization of the zeroth law of thermodynamics.

D b3. X_k-Reservoir or, briefly, reservoir [symbol: R]: An infinite thermodynamic system that can be coupled by X_k-exchange to finite systems in such a way as to make $e'(x_k' \mid x_\lambda')$ and $e''(x_k'' \mid x_\lambda'')$ statistically independent of each other. Within STE the specification of this exchange will provide an adequate description of the interaction of the system and reservoir. Two reservoirs are equivalent if the time-average of X_k transfer between them is zero when they are coupled to each other by the intermediary of a finite system.

P b2. The equivalence relationship explained in *D b3* is independent of the nature of the coupling system, provided that it does not inhibit the X_k-exchange. Moreover, the relation is transitive, that is, if a reservoir R' is equivalent to R'' and R'' is equivalent to R''', then R' is equivalent to R'''.

As an immediate consequence of this equivalence relationship, we state the corollary:

C b1. The class of equivalent X_k reservoirs can be labeled by a set of parameters $\theta_1, \theta_2, \cdots$, briefly θ_s, in such a way that equivalent reservoirs are labeled by the same set θ_s, while nonequivalent ones differ in at least one of the θ. Reservoirs will be denoted also as $R(X_k, \theta_s)$ or $R(\theta_s)$.

Evidently the labels θ_s are closely related to the intensities of MTE, but they constitute much more rudimentary qualitative concepts. They lack a definite scale; they are not necessarily paired with the X_k; and they are even unspecified as to their number. Thus, for example, in the case of thermal coupling we do not postulate the existence of a *single* parameter, the temperature. The intensities, in their quantitative thermodynamic meaning are to be derived from the theory.

Other immediate consequences of *D b3* and *P b2* are the following: Equivalent reservoirs can be united to form another reservoir of the same class; the class of a reservoir remains unaffected if any finite system is joined to it. Two nonequivalent reservoirs are to be joined only by the intermediary of a finite system. However, this situation does not lead to equilibrium and is outside the scope of the present theory.

P b3. Statistical Equilibrium of a Finite System and Reservoir. Consider an ensemble $e(x_k \mid x_\lambda)$ that has been coupled for a sufficiently long time to a reservoir $R(X_k, \theta_s)$. Then the probability that the X_k of a particular member of e be less than some value x_k is given by a unique, (cumulative) d.f. $F(x_k \mid x_\lambda, \theta_s)$ which is completely determined by the nature of the system, indicated by its fixed variables x_λ, and by the class of the reservoir, specified by the θ_s. Or in symbols[5]:

$$F(x_k \mid x_\lambda, \theta_s) = \Pr\{X_k < x_k \mid x_\lambda, \theta_s\}. \tag{1.5}$$

Expressions analogous to (1.2), (1.3), and (1.4) can be written down in obvious fashion. The function F is called the (*generalized*) *canonical* d.f. More precisely, the d.f., or the corresponding ensemble, is canonical in X_k and microcanonical in X_λ. The d.f. that is canonical only in U and microcanonical in all others is called *canonical* in the narrower sense of the word. The d.f. that is microcanonical in the volume and canonical in all other X's is called the *grand canonical* d.f. A single system whose behavior is represented by a canonical ensemble is called a canonical system, or, from the experimental point of view, a system in thermodynamic *equilibrium* with $R(\theta_s)$.

Finally, we formulate a stability property for the canonical d.f.

P b4. Consider two ensembles e' and e'' with the canonical distributions $F'(x_k' \mid x_\lambda', \theta_s)$ and $F''(x_k'' \mid x_\lambda'', \theta_s)$, respectively, although they need not be in contact with a reservoir. If the two ensembles are coupled member by member through walls $W[X_k]$ and then separated again into e' and e'', the reconstituted ensembles have the same canonical d.f.'s as the original ones.

This postulate might be regarded as a statistical "zeroth law"[6]: two ensembles that have been in statistical equilibrium with a reservoir are in statistical equilibrium with each other, regardless of the presence or absence of the reservoir.

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[5] In the literature, the vertical bar is used in the arguments of conditional probabilities. To the right of the bar are those random variables that assume fixed values for the events considered. Our use is somewhat more general, since θ_s are not random variables, but fixed properties of the reservoir. See also footnote 4.

[6] Cf. Thesis, pp. 37–38. More accurately: as the final element in the statistical generalization of the zeroth law begun in *D b3*. It can be shown that a similar law holds for any two objects ("object" being a canonical system, ensemble, or reservoir).

II. THE CANONICAL FORMALISM: SYSTEMS WITH A SINGLE RANDOM VARIABLE

A. Derivation of the Distribution Functions

The postulates of Section I allow one to derive the functional form of the generalized canonical d.f.: $dF(x_k \mid x_\lambda, \theta_s)$ and of the microcanonical d.f.: $d\mathfrak{F}(x_k' \mid x_k, x_\lambda', x_\lambda'')$. Although the discussion of the general case offers no formal complications, the conceptual interpretation of the formalism is greatly facilitated if the discussion is confined at first to the special case of the ordinary canonical d.f. in which the internal energy $X_1 = U$ is the only random variable of the system. We shall return in Section III to the general case of many variables.

Apart from a few refinements, we follow Szilard and analyze a simple sequence of thermodynamic operations on two ensembles and a heat reservoir, establish a functional equation involving dF and $d\mathfrak{F}$, and derive those solutions of this equation which satisfy the physical conditions of the problem.

We consider two ensembles $e'(x')$ and $e''(x'')$, and bring each member of e' into thermal contact with a member of e'' to form an ensemble of pairs of systems $e(x', x'')$. This ensemble of composite systems is then brought into thermal equilibrium with the reservoir $R(\theta_s)$. According to *P b3* and *D b3* the joint probability that the subsystems of a member of the ensemble e have the energies u' and u'' is

$$\Pr\{u' \leqq U' < u' + du', u'' \leqq U'' < u'' + du'' \mid x', x'', \theta_s\} \\ = dF'(u' \mid x', \theta_s)\, dF''(u'' \mid x'', \theta_s).$$

This d.f. persists, regardless of whether the contacts between the ensemble and R, and the contacts between the subensembles are maintained, (*P b4*). If, then, the ensemble e is decoupled from R, we can describe this same d.f. from a different aspect: The above joint probability appears as the probability $dF(u \mid x', x'', \theta_s)$ of finding the energy $u = u' + u''$ in a member of the composite ensemble, multiplied by the conditional probability $d\mathfrak{F}(u' \mid u, x', x'')$ that this energy splits in the desired fashion among the subsystems (*P b1* and *P b3*). The comparison of the two expressions yields the basic functional equation:

$$dF'(u' \mid x', \theta_s)\, dF''(u'' \mid x'', \theta_s) = dF(u \mid x', x'', \theta_s)\, d\mathfrak{F}(u' \mid u, x', x''). \quad (2.1)$$

This equation reduces to the well-known Boltzmann relation if the microcanonical d.f. is a δ-function, i.e., if

$$d\mathfrak{F}(u' \mid u) = \delta(u' - u_0) \quad (2.2)$$

where u_0 is the amount of energy that would be trapped in the system (x') if the principle of thermostatistic determinism of MTE were rigorously valid.

To solve (2.1) for the analytic forms of dF and $d\mathfrak{F}$ we shall need the logarithm of these functions. For this reason, we must first examine the nature of the zeros of the distribution functions. Suppose that the d.f. of e' vanishes for a particular set of values of the energy and of the parameters: $dF'(u_0' \mid x', \theta_{s0}) = 0$. There is, in general, no reason why $dF(u \mid x', x'', \theta_{s0})$ should be simultaneously zero. Therefore, from (2.1), $d\mathfrak{F}(u_0' \mid u, x', x'') = 0$. Since this relation is θ_s-independent, (2.1) requires that $dF'(u_0' \mid x', \theta_s) = 0$ hold independently of the values of θ_s.

Consequently, there must be a component in $dF'(u_0' \mid x', \theta_s)$ which is θ-independent and which is zero for the entire set of forbidden values of U'. We may, therefore, exclude this forbidden set from consideration for the present.[7] In similar fashion, we exclude the forbidden sets of U'' and U and, so, all zero-values of dF and $d\mathfrak{F}$.

Taking the logarithm of (2.1) and writing $u' + u''$ for u, we have:

$$\begin{aligned} \ln dF'(u' \mid x', \theta_s) + \ln dF''(u'' \mid x'', \theta_s) &= \ln dF(u' + u'' \mid x', x'', \theta_s) \\ &\quad + \ln d\mathfrak{F}(u' \mid u + u'', x', x''). \end{aligned} \tag{2.3}$$

Let c_s be an arbitrary but fixed set of values of the parameters θ_s, labeling some heat reservoir. We take, now, the difference between (2.3) for a general θ_s and (2.3) when evaluated at c_s. Introducing the notation

$$\eta(u, x, \theta_s, c_s) = \ln dF(u \mid x, \theta_s) - \ln dF(u \mid x, c_s), \tag{2.4}$$

we obtain

$$\eta'(u', x', \theta_s, c_s) + \eta''(u'', x'', \theta_s, c_s) = \eta(u' + u'', x', x'', \theta_s, c_s). \tag{2.5}$$

We shall now solve this functional equation under the simplifying assumption that η is a differentiable function of u.[8] Differentiating (2.5) with respect to u' at constant u'', and vice versa, we obtain

$$\frac{\partial \eta'(u', x', \theta_s, c_s)}{\partial u'} = \frac{\partial \eta(u' + u'', x', x'', \theta_s, c_s)}{\partial u'} = \frac{\partial \eta(u, x', x'', \theta_s, c_s)}{\partial u} \tag{2.6a}$$

$$\frac{\partial \eta''(u'', x'', \theta_s, c_s)}{\partial u''} = \frac{\partial \eta(u' + u'', x', x'', \theta_s, c_s)}{\partial u''} = \frac{\partial \eta(u, x', x'', \theta_s, c_s)}{\partial u} \tag{2.6b}$$

Expression (2.6a) is evidently independent of x'' and (2.6b) of x'. Since the

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[7] That such forbidden sets exist is evident from the discrete energy spectra of quantum mechanics.

[8] This assumption may seem incongruous with the fact that the energy is, in general, defined only on a discontinuous set. However, the continuous solutions of (2.5) can be subsequently restricted to the allowed energy spectrum and, therefore, our procedure yields satisfactory solutions of (2.1). On purely mathematical grounds, Eq. (2.5) also has more general solutions but these can be excluded by physical considerations. At any rate, we shall see in Section II, B that the analytical character of the function $\eta(u)$ is consistent with the discontinuous aspects of the problem.

two expressions are equal, they cannot depend on the nature of the systems (x') and (x''), but only on θ_s and c_s. Denoting this universal function of the reservoir properties as $-B(\theta_s, c_s)$, we obtain after integration

$$\eta(u, x, \theta_s, c_s) = -B(\theta_s, c_s)u - A(x, \theta_s, c_s) \tag{2.7}$$

with similar relations for η' and η''. Inserting these expressions into (2.5) we see that the integration constants A are additive

$$A'(x') + A''(x'') = A(x). \tag{2.8}$$

From (2.7) and (2.4) we obtain

$$\ln dF(u \mid x, \theta_s) = \ln dF(u \mid x, c_s) - A(x, \theta_s, c_s) - B(\theta_s, c_s)u.$$

Since the left-hand side is independent of c_s, each term on the right must be individually separable into a term containing c_s and one not containing it, in such a way that the c_s-dependent terms cancel.[9] Designating the portions of dF, A, and B that are independent of c_s as dG, Φ, and β, respectively, we have the general solution of (2.1)

$$dF(u \mid x, \theta_s) = dG(u, x)e^{-\Phi(x,\theta_s)-\beta(\theta_s)u} \tag{2.9}$$

with

$$\Phi'(x', \theta_s) + \Phi''(x'', \theta_s) = \Phi(x, \theta_s). \tag{2.10}$$

Our derivation holds only for those values of u that have a nonvanishing probability. But we may now bring back the forbidden values of u, defining $dG(u_0) \equiv 0$.

The condition on normalization of the probability dF leads to

$$e^{\Phi(x,\theta_s)} = \int_u e^{-\beta(\theta_s)u}\, dG(u, x), \tag{2.11}$$

where the integration extends over the entire range of u. Evidently this integral, and hence $\Phi(x, \theta_s)$, depends on the set of θ_s only through the intermediary of the single parameter β, and the canonical d.f. can be written in the form[10]

$$dF(u \mid \beta) = dG(u, x)e^{-\Phi-\beta u} = dG(u, x)e^{-\beta u}Z^{-1}(\beta, x), \tag{2.12}$$

where

$$\ln Z(\beta, x) = \Phi(\beta, x). \tag{2.13}$$

We see that the canonical distribution function dF is the product of three factors. One factor depends only upon the type of system and its energy; a

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[9] A formal proof of this plausible statement is straightforward but tedious.

[10] We shall soon see that β is a satisfactory parameter for labeling reservoirs as stipulated in *C b1*. Therefore we shall henceforth use the parameter β without further regard to the θ_s.

second depends upon the type of system and the reservoir parameter β; the third is an exponential function that provides the coupling between u and β in a manner the same for every system.

With these facts established, we may, as a rule, omit explicit reference to the fixed variables x. In particular, we rewrite the normalization condition (2.11) as

$$Z(\beta) = \int_u e^{-\beta u}\, dG(u). \tag{2.14}$$

Moreover, from (2.10) and (2.13),

$$Z'(\beta)Z''(\beta) = Z(\beta) \tag{2.15}$$

The function $Z(\beta)$ is seen to be the Laplace-Stieltjes transform of $G(u)$. The requirement that the integral (2.14) exist imposes limitations on the ranges of β and u which we shall consider later. The use of Stieltjes integrals is convenient for handling the mixed, discrete-continuous energy spectrum of quantum mechanics. But if $G(u)$ is differentiable or varies in value only discontinuously, one has for sufficiently small energy intervals,

$$dG(u) = g(u)du, \tag{2.16a}$$

or

$$dG(u) = g(u_n) = g_n \tag{2.16b}$$

and (2.14) reduces to the more usual form of the Laplace (-Riemann) transform or to a sum respectively. Corresponding changes are brought about in the d.f. (2.12).

We shall call $G(u)$ the *structure function* of the system. This use is close to that of Khinchin (*11*) who calls $g(u)$ the structure function. $Z(\beta)$ will be referred to as the *generating function* or *partition function*.

Inserting (2.12) into (2.1) and using (2.15), we obtain the microcanonical d.f.

$$d\mathfrak{F}(u' \mid u) = dG'(u')dG''(u - u')/dG(u) \tag{2.17}$$

which is independent of β as it should be. The normalization of this probability yields

$$dG(u) = \int_{u'} dG'(u')\, dG''(u - u'). \tag{2.18}$$

Thus the composition of the structure functions of independent systems is obtained by convolution or "faltung." It is well known from the theory of the Laplace transform that this rule is equivalent to the product rule of composition (2.15) for the generating function.

B. FORMAL PROPERTIES OF THE CANONICAL DISTRIBUTION

Before turning to the physical interpretation of the functions and parameters appearing in the canonical d.f., it is convenient to summarize some of the mathematical implications of the formalism.

From the theory of the Laplace transform, we know that if $Z(\beta)$ converges for one value of β, it will converge for all larger values of β (*12*, p. 37). The limit of convergence depends on the nature of the function $G(u)$. We shall return to this point below. Within the range of convergence of (2.14) $Z(\beta)$ is analytic (*12*, p. 57); thus it possesses finite derivatives of all orders. Therefore we obtain the canonical averages

$$\frac{d^n Z}{d\beta^n} = \int (-u)^n e^{-\beta u}\, dG(u) = (-)^n \overline{u^n} Z. \tag{2.19}$$

We shall need the important expressions for the average and the variance of the energy:

$$\bar{u} = -\partial\Phi/\partial\beta \tag{2.20}$$

$$\operatorname{Var} u = \overline{(u - \bar{u})^2} = \overline{(\Delta u)^2} = \partial^2\Phi/\partial\beta^2 > 0. \tag{2.21}$$

Strictly speaking, the inequality sign in this important convexity relation should be $\geqq 0$. It is, however, a simple matter to show that the variance of the canonical d.f. can vanish only in the limiting case in which all members of the ensemble are in the ground state (*P a6*).

For a given value of $\bar{u}$, Eq. (2.20) can be considered as an equation for the unknown β. For systems with an unbounded energy spectrum $\bar{u}$ is itself unbounded. It follows from the convexity of $\Phi = \Phi(\beta)$ that Eq. (2.20) has a single positive solution, $\beta = \beta_0$, for any positive $\bar{u} = u_0$ (*11*, p. 77). Thus we have established a one-to-one relation between the average ensemble energy $\bar{u}$ and the reservoir parameter β. Moreover, from (2.20) and (2.21), we have

$$d\bar{u}/d\beta < 0. \tag{2.22}$$

Thus if an ensemble $e(X)$ is brought in contact at first with the reservoir $R(\beta_1)$ and then with $R(\beta_2)$ where, say, $\beta_1 < \beta_2$, then the canonical averages satisfy the relation

$$\bar{u}(\beta_1) > \bar{u}(\beta_2). \tag{2.23}$$

Therefore the contacts mentioned will bring about an energy flow from $R(\beta_1)$ to $R(\beta_2)$.

Thus we see that β is a satisfactory parameter for labeling reservoirs in the sense of *C b1*. Of course, in addition, β has more specific properties and provides a numerical measure for the intuitive concept of the temperature, higher

β's corresponding to lower temperatures. This is not trivial, since our definition of the reservoir parameters did not specify a direction of the flow for the X_k or their averages between different reservoirs. Moreover, β has an "absolute" character in the sense that it is uniquely determined once the unit of energy is fixed and does not depend on the nature of the system chosen as the basis for the canonical ensemble or on any other arbitrary convention. Nevertheless, we are still not in a position to establish the connection between β and the thermodynamic temperature. This is possible only through the concept of entropy which has not yet been defined.

The canonical formalism exhibits an interesting duality. The properties of a particular ensemble $e(x)$ can be described either in terms of the generating function $Z(\beta, x)$ or in terms of the structure function $G(u, x)$ with the reservoir parameter β specified in addition. Either of these descriptions allows us to arrive at the other by means of the Laplace transformation or its inverse. The exponential kernel of this transformation corresponds physically to the coupling of the system and the reservoir.

Although we have two equivalent representations for canonical ensembles, these descriptions are far from symmetric, and the functions $Z = Z(\beta, x)$ and $G = G(u, x)$ play different roles in the conceptual structure of the theory. As we shall see in Section II,C, the elaboration of the properties of the former enables us to establish contact with MTE, whereas the latter is a connecting link with quantum mechanics. Moreover, the two representations exhibit also a formal mathematical asymmetry.

The "moment-generating function" $Z(\beta)$ is extremely smooth, with continuous derivatives of all orders in its interval of convergence. These derivatives provide the successive moments of the canonical d.f. as shown in (2.19). In contrast, G is usually discontinuous, corresponding to the quantum-mechanical discrete spectrum of the system. This discontinuous character of the structure function was taken into account in our solution of the functional equation (2.1). As a result, the assumption that $\eta(u, \beta)$ should be differentiable yielded the form

$$\eta(u, \beta) = -u\beta - \ln Z(\beta) \tag{2.26}$$

which is consistent with the discontinuous character of $G(u)$. We note that Szilard's method of solution required the differentiability of $G(u)$.

C. Structure Function and Entropy

The discussion of Section B is of a purely formal nature. In order to develop the physical interpretation of the theory, first, we connect the present formalism with that of quantum mechanics and, thus, pave the way for the microscopic calculation of the thermodynamic functions; second, we shall derive the formalism of MTE from the present basis and, thus, establish the connection of STE with experiment.

One simple postulate will do much toward joining STE and quantum mechanics.

P c1. The structure function $G(u, x)$ is to be interpreted as the number of linearly independent solutions of the Schrödinger equation which have an energy eigenvalue $E \leqq u$ under the condition that x be constant. These solutions are the possible microstates of the system and have equal *a priori* probabilities.

Accordingly, the canonical d.f. (2.12) can be written in the alternative forms:

$$f_n = g_n(x)e^{-\Phi-\beta u_n}, \tag{2.27a}$$

$$f_i = e^{-\Phi-\beta u_i}, \tag{2.27b}$$

where f_n is the probability of a g_n-fold energy level u_n and f_i is the probability of a single microstate of energy u_i.

It is easy to see that *P c1* is consistent with the properties of the structure function, in particular with the composition rule (2.18). Otherwise, this postulate is justified only by its success, which is considerable since *P c1* allows us to integrate with the present theory most quantum-statistical calculations of the structure functions of particular systems.

We are in a position now to specify the physical criteria for the numerical range of β. The various types of degrees of freedom give rise to two kinds of structure function, distinguished by their asymptotic behavior for high energies. For translational, rotational, and vibrational degrees of freedom, $G(u) \sim u^{\mathfrak{N}/2}$ where $\mathfrak{N}$ is the number of degrees of freedom. For internal angular momentum, $G(u)$ is bounded. Whence it is evident that $Z(\beta)$ converges for all positive values of β for all physical systems. Moreover, since all physical systems have at least one kind of degree of freedom with an unbounded spectrum, $Z(\beta)$ diverges for $\beta \leqq 0$.

There are, however, certain physical situations for which it is convenient to consider a particular degree of freedom as a thermodynamic system in its own right. For example, one may treat a spin system as a thermodynamic system, in spite of the fact that it occupies the same space as the crystal lattice, contrary to the requirement that thermodynamic systems be disjoint regions in space (*D a1*). For such "systems" $G(u)$ is bounded and β can be negative. We shall return to the interpretation of this situation in Section IV,B.

We turn now to the problem of establishing the connection of STE with MTE. The key to this problem is contained in the dualism of the canonical formalism pointed out in Section II,B. It is evident that the analytic function $Z = Z(\beta, x)$ and, hence, $\log Z \equiv \Phi(\beta, x)$, contains all statistical information about the system. As seen in (2.15), moreover, Φ is additive for independent systems and obeys the convexity relation (2.21). This fact allows us to establish a very smooth junction of the present theory with MTE. The latter theory is centered around the so-called fundamental equations, which are certain additive functions each of which contains all thermostatic information about the system. The various fundamental equations are associated with different physical situations. The one associated with a system in energy-exchange with a heat reservoir (the static equivalent of the canonical situation) is described in terms of the Massieu function[11]

$$\Psi(1/T, x) = S - U/T \tag{2.28}$$

where S, U, T are the thermostatic entropy, energy, and temperature. Hence we have to require that the $\Phi(\beta, x)$ of the present theory be proportional to the statistical counterpart of the Massieu function

$$\Psi = k\Phi(\beta, x). \tag{2.29}$$

The convexity relation (2.21) ensures the validity of the proper extremal properties of Ψ; and the postulates of MTE are satisfied for our construction of the fundamental equation. Thus the junction of MTE and STE is, in principle, completed for the limited choice of independent variables, and we could build up MTE from the basis of STE.

We seek now the formulation of the concept of entropy appropriate to the present canonical theory. In MTE the entropy is defined as that fundamental equation which is appropriate for isolated systems. Such a definition will be introduced in Section IV along with a complete and physically meaningful formalism for isolated systems; here we must seek another approach.[12] That different concepts of entropy are required for canonical and isolated systems is to be expected in a theoretical structure where such systems are no longer regarded as equivalent.

Guided by the thermostatic limit, given in (2.28), we define the canonical entropy as

$$\bar{s} = k\Phi - k\beta\frac{\partial\Phi}{\partial\beta} = k(\Phi + \beta\bar{u}) = -k\beta^2\frac{\partial(\Phi/\beta)}{\partial\beta}. \tag{2.30}$$

Since Eq. (2.20) enables us to express $\bar{u}$ and β in terms of one another, we have the option of considering $\bar{s}$ as a function of $\bar{u}$, corresponding to a fundamental equation of MTE, or as a function of β, as is more natural in the canonical formalism. The former alternative leads at once, through the Legendre transformation of $\bar{s}$, to a number of important thermostatic relations.

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[11] Systems coupled with heat reservoirs can be described in terms of the Helmholtz function or the Massieu function. In the scheme based on the former, the virtual processes are (reversible) entropy transfers; in the latter, energy transfers.

[12] Thus, our problem here is the inverse of that encountered in statistical mechanics; there one starts with an isolated system, and the problem is that of transition to coupled and open systems.

Differentiating (2.30) at constant x, we obtain

$$d\bar{s} = k\,d\Phi + k\bar{u}\,d\beta + k\beta\,d\bar{u} = k\beta\,d\bar{u} \equiv d\bar{u}/T. \tag{2.31}$$

Hence,

$$\beta = \frac{1}{k}\left(\frac{\partial \bar{s}}{\partial \bar{u}}\right)_x = \frac{1}{kT} \tag{2.32}$$

where T is defined by (2.31). It is evident from our previous discussion of β and from (2.31) that T has all the properties of the absolute thermodynamic temperature.

Moreover,

$$k\Phi = \bar{s} - \bar{u}/T = -A/T, \tag{2.33}$$

where $A = A(T, x)$ is the Helmholtz free energy.

The convexity relation (2.21) for Φ, together with (2.20) and (2.32), yields the convexity relation for $\bar{s}$:

$$\partial^2\bar{s}/\partial\bar{u}^2 \leqq 0. \tag{2.34}$$

Expression (2.30) suggests the definition of a random function

$$s(u, \beta, x) \equiv k[\Phi(\beta, x) + \beta u]. \tag{2.35}$$

This function figures prominently in Gibbs' discussion of the extremal properties of the canonical ensemble and was called by him the index of probability; we shall call it the entropy function. Of course, the entropy proper is not a random function, but a property of the ensemble. With this fact in mind, there is no objection to this terminology, the advantages of which will be apparent in the next section. In case of ambiguity we shall refer to (random) entropy function and to average entropy, respectively.

From (2.35) and (2.12) we obtain

$$\bar{s} = k \int dF(u) \ln\,[dG(u)/dF(u)] \tag{2.36}$$

or, in the case of a discrete spectrum, by using (2.27), we have

$$\bar{s} = -k \textstyle\sum_i f_i \ln f_i\,. \tag{2.37}$$

Equations (2.36) and (2.37) are well-known and important relations which suggest a generalization of the entropy concept.

Let us consider a system the nature of which is specified, either in terms of the structure function $G(u, x)$ or in terms of its set of microstates. If the system is not in equilibrium, its state might be describable in terms of ensembles other than canonical. Suppose in the corresponding d.f. the probability of the microstate i is ϕ_i with

$$\textstyle\sum_i \phi_i = 1. \tag{2.38}$$

It is usual to define the functional

$$s^{(\phi)} = -k \textstyle\sum_i \phi_i \ln \phi_i \tag{2.39}$$

as the entropy of the d.f. ϕ.

It is easy to show by the method of Lagrange multipliers that, among all normalized distributions having the same average energy, the average entropy takes on its maximum value for the canonical d.f.

$$s^{(\phi)} \leqq \bar{s} = k(\Phi + \beta\bar{u}) \tag{2.40}$$

or from (2.33)

$$\bar{u} - s^{(\phi)}T - A \geqq 0, \tag{2.41}$$

where the equality sign is valid only if $s^{(\phi)}$ is the canonical average entropy.

Relation (2.41) is formally similar to the extremum principle (5.20) in (MTE). Yet the two principles differ essentially because they refer to different comparison states. The noncanonical d.f.'s ϕ are not definable in MTE even as virtual states. We shall return to this matter in the next section. The fact that the canonical d.f. maximizes the entropy functional of a class of d.f.'s has also been used as a particularly direct method of derivation of this d.f. (*5*). We shall discuss the relation of this procedure to ours in Section VI.

III. THE CANONICAL FORMALISM FOR SEVERAL RANDOM VARIABLES

A. The Canonical Distribution Function

We proceed now to generalize the developments of Section II to several random variables.

We consider two ensembles $e'(x_k' \mid x_\lambda')$, $e''(x_k'' \mid x_\lambda'')$ coupled to a reservoir by means of the simultaneous exchange of the several quantities X_k. We stipulate that the volume be fixed, and the fluctuation confined to that of energy and mole numbers. The d.f. to be derived is thus the grand canonical d.f.[13]

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[13] Although the theory can be applied without difficulty to the case of simultaneous random exchanges of volume and energy through diathermic pistons, this case is of slight importance in comparison with the diffusive coupling leading to the grand canonical d.f. On the other hand, an adiabatic piston produces mechanical accelerations and, hence, dynamic correlations, which cannot be accounted for on the present postulational basis, since the final equilibrium state depends upon such mechanical detail. The sweeping exclusion of processes involving random volume-changes saves us the trouble of hedging the general statements with complicated qualifications.

The simultaneous exchange of several quantities X_i between two systems (x') and (x'') can be represented as a vector $\{\delta x_1', \delta x_2', \cdots\}$ that is equal and opposite to $\{\delta x_1'', \delta x_2'', \cdots\}$. In this vector space we can choose a set of linearly independent vectors or, rather, directed lines (rays):

$$\delta x_i' \neq 0, \qquad \delta x_k' = 0, \qquad k \neq i \quad (3.1)$$
$$i = 1, 2, \cdots$$

the linear combinations of which represent all exchange processes. The basic processes (3.1) can be physically realized, although not necessarily by a simple application of walls.[14]

The derivation of the canonical d.f. can be carried out in such a step-by-step analogy to Eqs. (2.1)–(2.12) that we confine ourselves to giving the final answer with a few explanatory remarks. The crucial point in the argument is that the many-variable analog of Eq. (2.5) can be independently differentiated with respect to the x_i of Eq. (3.1). The term "independent" has many meanings and it may be worth while to point out that our basic processes are not dynamically independent, since we made no special assumptions on the system; they are not even statistically independent as will be evident from (3.6).[15] What we mean is that the virtual-exchange processes form a linear manifold because the X_i are additive invariants (*P a1*, *P a2*). Such a manifold can be spanned by linearly independent basis vectors; this is all that we need for the derivation of the final result:

$$dF(x_i \mid x_\lambda, \pi_i) = dG(x_i, x_\lambda) \exp\left[-\Phi_{x_\lambda}(\pi_i) - \sum \pi_i x_i\right], \qquad (3.2)$$

where $G(x_i, x_\lambda)$ is the structure function, Φ and the π_i are parameters of the

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[14] Thus, the process $\delta u' = 0$, $\delta n' \neq 0$ cannot be automatically ensured by walls. Mass transfer is always coupled to energy transfer, and $\delta u' = 0$ can be achieved only by carefully compensating for the energy transferred with the mass by producing heat flow in the opposite direction.

[15] In the microscopic sense the transfer processes exhibit a definite coupling pattern. Thus an individual transfer of a particle transfers also a fixed amount of energy. This coupling of the fluxes plays a central role in irreversible thermodynamics (*14*). However, the d.f. (3.2), that ignores the temporal sequence in the variation of the x_i, contains this coupling effect only in a strongly averaged form through the dependence of the function Φ_{x_λ} on all the $\pi_1, \pi_2, \cdots$. There is one striking exception in which the coupling between the δx_i essentially affects the equilibrium situation. In liquid helium II, a very thin capillary acts as an entropy filter; it is restrictive of entropy and of excitation energy, but unrestrictive of mass flow. The energy carried along with the latter is that of the ground state. Thus in this case we have a perfect coupling between the exchange of volume, mass, and energy. Two containers of helium coupled by such a capillary may have different temperatures, provided that they have correspondingly different pressures. The situation can be handled by thermostatic methods as shown (*MTE*, p. 38).

d.f., and the π_i are functions of the original θ_s which they completely replace. The canonical d.f. (2.12) is a special case of (3.2); hence, assuming $x_1 = u$, we have $\pi_1 = \beta$.

The implications of the d.f. (3.2) are so similar to those obtained in the one-variable case that we shall merely list the most important formulas. The normalization of the probability (3.2) yields

$$\int_{x_i} dG(x_i, x_\lambda) \exp\left[-\Phi_{x_\lambda}(\pi_i) - \sum \pi_i x_i\right] = 1. \tag{3.3}$$

The partition function is

$$Z_{x_\lambda}(\pi_i) \equiv \exp\left[\Phi_{x_\lambda}(\pi_i)\right] = \int_{x_i} dG(x_i, x_\lambda) \exp\left(-\sum \pi_i x_i\right). \tag{3.4}$$

Differentiating (3.3) with respect to π_i, we have

$$\bar{x}_i = -\partial\Phi/\partial\pi_i . \tag{3.5}$$

A second differentiation yields at once the covariances

$$\overline{\Delta x_i \, \Delta x_j} = \frac{\partial^2\Phi}{\partial\pi_i \, \partial\pi_j} \equiv \Phi_{ij} \qquad i, j = 1, 2, \cdots, \tag{3.6}$$

where $\Delta x_i = x_i - \bar{x}_i$.

The diagonal elements of the matrix $\| \Phi_{ij} \|$ of the covariances are obviously nonnegative:

$$\overline{(\Delta x_i)^2} = \partial^2\Phi/\partial\pi_i^2 = -\partial\bar{x}_i/\partial\pi_i \geqq 0, \tag{3.7}$$

where the limiting case of zero variance holds only when the random variable X_i is actually fixed, and there is no statistical problem—a situation that arises in the limiting case of absolute zero. The statement embodied in (3.7) can be immediately sharpened: the matrix $\| \Phi_{ij} \|$ must be positive semidefinite, since otherwise a transformation of the variables would lead to negative diagonal elements.

Equation (3.7) implies, as in the one-variable case, that, for reservoirs of different π_i but with all other π_j equal, $\pi_i' < \pi_i''$ requires $\bar{x}_i' > \bar{x}_i''$. Hence X_i will flow, on the average, from $R'(\pi_1, \cdots \pi_{i-1}, \pi_i', \pi_{i+1}, \cdots)$ to $R''(\pi_1, \cdots \pi_{i-1}, \pi_i'', \pi_{i+1} \cdots)$ when both are coupled to the same finite system. But no general statements hold for the direction of fluxes between reservoirs differing in two or more of the π_i.

We turn to the identification of the thermostatic functions in terms of the general canonical d.f. The situation continues to parallel the one-variable case. In analogy to (2.35) we define the random entropy function

$$s(x_i, \pi_i, x_\lambda) = k\left[\Phi_{x_\lambda}(\pi_i) + \sum \pi_i x_i\right]. \tag{3.8}$$

The canonical average entropy is

$$k(\Phi + \sum \pi_i\bar{x}_i) = k(\Phi - \sum \pi_i\partial\Phi/\partial\pi_i) = s(\bar{x}_i, \pi_i, x_\lambda) = \bar{s}. \qquad (3.9)$$

By using Eq. (3.5), we can express the π_i by the $\bar{x}_i$ or vice versa. The condition of solubility is

$$\det |\Phi_{ik}| = \frac{\partial(\bar{x}_1, \bar{x}_2, \cdots)}{\partial(\pi_1, \pi_2, \cdots)} \neq 0. \qquad (3.10)$$

As we have pointed out above, this relation is satisfied except at absolute zero. Another singularity of the theory arises at critical states, for which the determinant (3.10) becomes infinite. For a further discussion of these singularities we refer to (MTE). Equation (3.6) contributes the additional information that at critical states the fluctuations become infinite. While critical fluctuations are indeed very large, they cannot, of course, be infinite in a finite system. We return to this point in Section IV,E.

We define now new intensity parameters

$$P_i = -kT\pi_i \qquad i = 2, 3, \cdots. \qquad (3.11)$$

Comparison with the canonical d.f. yields:

$$P_1 = T = (k\,\pi_1)^{-1} \qquad (3.12)$$

By introducing a notation used in (*MTE*) we have

$$-kT\Phi_{x_\lambda}(\pi_i) = \bar{u} - T\bar{s} - \sum{}' P_i\bar{x}_i \equiv \bar{u}[T, P_i]. \qquad (3.13)$$

In particular, we obtain for the important grand canonical ensemble,

$$\Omega(V, T, \mu_j) \equiv -kT\Phi_v(T, \mu_j) = \bar{u} - T\bar{s} + \sum \mu_j n_j \qquad (3.14)$$

where μ_j is the chemical potential of the jth component. If the volume is a random variable, the corresponding intensity, is, of course, the negative of the pressure.

The formulas (2.36)–(2.39) remain unchanged in the many-variable case, provided only that expression (3.2) is used for the d.f. The maximum principle (2.40) is generalized to

$$\bar{u} - \langle s\rangle_\varphi T - \sum{}' P_i\bar{x}_i - \bar{u}[T, P_i] \geqq 0. \qquad (3.15)$$

The equality sign is valid if and only if φ is the canonical d.f. (3.2).

We conclude this section with a few remarks concerning the range of the intensities π_i, inferred from the condition that the integral (3.4) be convergent. Since the structure function increases, at most, algebraically (power law) for large x_i, all positive values are admissible for the π_i. Zero and negative values are admissible as well if the structure function is bounded. Thus, the existence of a bounded $G(v)$, u = constant, for condensed phases indicates at once the possibility of negative pressures. If, as discussed above with reference to energy and mass transfer, δx_i cannot be kept zero when $\delta x_j \neq 0$, this fact must be considered in evaluating the ranges of the π_i. Thus, in the case of Fermi statistics, positive values of the chemical potential are possible because the high-density states have a sufficiently high energy to ensure the convergence of the integral (3.4).

B. PERFECT GASES

The foregoing developments allow us to derive all of the quantitative information about a system that falls within the scope of STE and MTE, provided only that the structure function is obtained by solution of the Schrödinger equation. However, for systems of many degrees of freedom, this problem is usually insoluble. An effective way of overcoming this difficulty is to consider, at least as a point of departure, particularly simple systems called perfect gases. In statistical thermodynamics a perfect gas is defined as a system consisting of statistically independent constituents. As we have seen (Section II) the partition sum of such a system is the product of the partition sums of its parts. If the latter are sufficiently simple, the problem is easily manageable.

From the mechanistic point of view *statistical independence* is traced to *dynamic independence*: the perfect gas is an assembly of noninteracting particles. This simple connection was upset by quantum statistics. It became apparent soon enough that the dynamic independence of particles is no longer *sufficient* for statistical independence if the wave function of the system is subject to symmetrization (or antisymmetrization). However, it was recognized only gradually, as perfect-gas methods proved effective beyond all expectations in describing fluids of strongly coupled particles that dynamic independence is not *necessary* for statistical independence.

As we have pointed out, the requirement calling for the symmetrization of their wave functions renders *particles* unsuited to play the role of statistically independent elements for the building up of a gas. However, this role may be taken over by the single-particle *states*. In a fixed volume surrounded by impermeable walls these states will be spatially localized standing waves with characteristic energies ϵ_ν.

The total energy of the system is

$$U = \sum n_\nu \epsilon_\nu \tag{3.16}$$

where the occupation numbers n_ν are random variables. We have here, obviously, a transition from particles to fields. There is also a similarity to the definition of the composite system, only here the states are not spatially disjoint, but occupy the same volume. That they are, nonetheless, statistically independent is precisely what distinguishes a perfect gas from other systems. Thus the partition sum of the system will be

$$Z = \prod_\nu z_\nu \tag{3.17}$$

with

$$z_\nu = \sum_{n_\nu} x_\nu^{n_\nu} \tag{3.18}$$

and

$$x_\nu = e^{-\pi_1 \epsilon_\nu - \pi_2} = e^{(\mu - \epsilon_\nu)/kT}. \tag{3.19}$$

The summation is over 0 and 1 for Fermi-Dirac (F–D) statistics and over all nonnegative values of n_ν for Bose-Einstein (B–E) statistics.

Hence, we obtain

$$\varphi_\nu = \ln z_\nu = (1/\gamma) \ln (1 + \gamma x_\nu), \qquad \text{with } \gamma = \begin{cases} +1 & \text{F–D.} \\ -1 & \text{B–E} \end{cases} \tag{3.20}$$

The average occupation number is

$$\bar{n}_\nu = -\frac{\partial \varphi_\nu}{\partial \pi_2} = \frac{1}{e^{(\epsilon_\nu - \mu)/kT} + \gamma} = \frac{1}{(1/x_\nu) + \gamma}. \tag{3.21}$$

An interesting limiting case is obtained if

$$e^{-\mu/kT} \gg 1, \tag{3.22}$$

where the lowest energy was chosen to be zero. Now the two distributions degenerate into a common distribution

$$\begin{aligned} \varphi_\nu &= \ln z_\nu \longrightarrow x_\nu \\ \bar{n}_\nu &= x_\nu . \end{aligned} \tag{3.23}$$

Equation (3.23) can be rewritten as

$$\varphi_\nu = x_\nu = \ln e^{x_\nu} = \ln \left(1 + x_\nu + \frac{x_\nu^2}{2!} + \cdots \right) \tag{3.24}$$

and given a verbal formulation which is the well-known correction procedure for introducing the identity of particles into Boltzmann statistics.

The reason that we survey these well-known results is to show that they appear in a perspective that is different from the one of historical evolution. In the present context, Boltzmann statistics is the common degenerate limit of F–D and B–E statistics. Traditionally, however, the appearance of quantum effects is designated as "degeneracy," a usage which conflicts with every other accepted meaning of this term.

Finally, we note that the chemical potential in a B–E gas is negative (under the assumption that the lowest energy is zero). No sign restriction exists for F–D statistics. This is in agreement with the general rule stated at the end of Section III,A.

IV. THERMODYNAMIC THEORY OF MEASUREMENT

A. THE CLASSIFICATION OF THERMODYNAMIC EXPERIMENTS

The canonical d.f.'s contain three types of variables and, accordingly, enable us to consider three types of experimental questions.

(i) The response x_i of a known system (X_λ) is studied when in equilibrium with a reservoir $R(\pi_i)$ of known intensities ($X_\lambda, \pi_i \rightarrow x_i$).

(ii) Information on the properties of an unknown environment is sought through measurements performed on a system with which it is in equilibrium ($X_\lambda, x_i \rightarrow \pi_i$).

(iii) The investigation seeks the unknown aspects of the system from its response when it is in equilibrium with a known environment ($x_i, \pi_i \rightarrow X_\lambda$).

First let us consider briefly the macroscopic approach of (MTE) to the aforementioned experimental questions. Question type (i) corresponds to the measurement of, say, energy U and volume V, in environments of given temperature and pressure. Measurements of this sort lead to the determination of the equations of state and of the fundamental equation, except for the fact that only differences rather than absolute values of entropy are obtained.

In experiments of type (ii), one measures, say, the energy of a finite system and infers the temperature of the environment with which it has been in equilibrium. The finite system can be considered as a thermometer. The "indicator property," such as the length of a fluid column, can, of course, be calibrated in terms of energy differences. Whereas the discussion of diverse indicator properties is very important from the practical point of view, only the energy measurement is significant in the present context. Similar types of measurement, involving other variables, are frequent and often of more than routine interest. Thus the system might be a fossil object, the isotopic composition of which is used to infer the temperature and the composition of the archaic ocean from which it was deposited (*16*).

Finally, type (iii) experiments belong to chemistry, in which the responses of an unknown system to known chemical environments are used for the chemical analysis of the system.

Our problem, now is, to reconsider the three types of experimental questions from the point of view of STE. An experiment of type (i) can be easily interpreted in probabilistic terms. The intensities π_i and the X_λ determine the d.f. and, hence, the averages and the higher moments of the random variables x_i.

Within the context of MTE, the principle of thermostatic determinism (*MTE*, p. 62) asserts that the intensities of the environment uniquely determine the extensive quantities within the finite system and vice versa, provided that the system is in equilibrium with the environment. Considering systems at constant volume, we may say that the intensities of the environment and the densities of the system are uniquely *matched* with each other in equilibrium. Of course, within STE this deterministic connection is weakened into a statistical one. Whence, in questions of type (ii), we attempt to infer the parameters of the d.f. from the measured values of the random variables. This inverse of the usual probabilistic problem is called the problem of parameter estimation, and is dealt with in mathematical statistics. Mandelbrot (*4*) seems to have been the first to point out that parameter estimation is the proper counterpart to thermometry. He called the procedure *retrodiction*,[17] and identified the method of estimation that is implicit in the existing techniques of statistical mechanics as the "method of maximum likelihood" (*18*).

The suggestion that the methods of mathematical statistics be used within the context of basic theory might produce, at first blush, some apprehension. The inversion of probability calculus has by no means the uniqueness of, say, the inversion of differentiation. Hence the problem of retrodiction is beset by ambiguities and disputes. However, our use of estimation theory is not affected by these difficulties. We shall show in Section IV,B that the application of the method of maximum likelihood to the canonical d.f. is very simple and can be justified also on the basis of physical plausibility.[18] We refer to the statistical literature for its additional justification in terms of its desirable mathematical properties (*18*).

The results obtained will be used in Section IV,C to develop a statistical thermodynamics that applies to isolated systems and is the counterpart of the probabilistic interpretation of the canonical formalism that refers to open systems.

Questions of type (iii) are outside the scope of classical statistical physics, but they can be handled successfully within quantum mechanics (*6*). We shall show

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[17] This terminology may not be the best; it is to be understood only as a designation of the procedure to be described, and a number of possible connotations are to be avoided. Thus, the term was used by Watanabe (*17*) in the sense of inferring past observations from present observations, which would make retrodiction the symmetric inverse of prediction. The symmetry between prediction and retrodiction in analytic dynamics is so complete that it did not seem worth while even to discuss retrodiction. This may well be the origin of the widespread but unwarranted belief that science deals only with predictions. In order to emphasize the asymmetry, one might speak of *reconstruction* instead of retrodiction. Thus one reconstructs a sequence of events from a photographic plate taken in a bubble chamber. Jaynes (*5*) calls this procedure *interpretation*.

[18] One may note, however, that estimation-theoretical formalisms built on the microcanonical d.f. *are* beset by difficulties (cf. Thesis, p. 110) and, consequently, are of little use.

in Section IV,D that Nernst's law allows us to draw inferences with respect to experiments of type (iii). In Section IV,E we shall use the microcanonical ensemble to describe situations in which the finite size of the environment is significant.

B. THE MEASUREMENT OF INTENSITIES AS PARAMETER ESTIMATION

We consider a single finite system that is to represent a thermometer. This system is brought into equilibrium with a reservoir $R(\beta)$, the temperature β^{-1} of which is unknown. The measurement consists in separating the system from $R(\beta)$ and ascertaining its energy u. Since the system is finite, it represents an ideal measuring device insofar as its coupling with the infinite reservoir does not affect the temperature of the latter.

The next step in our procedure is to estimate the value of β from the knowledge of u. The available data are clearly insufficient for certitude in this respect, since we have no way of knowing whether u is equal to $\bar{u}$. In particular, *P b3* precludes the system from retaining any more memory of the reservoir temperature than that contained in the energy measurement.

Let us consider a measurement of the set of instantaneous values x_i for a system in contact with a reservoir $R(\pi_i)$ as the specification of a member of a canonical ensemble. Then the probability for finding this set of values is the d.f. (3.2). We now propose to consider dF as a function of the π_i for these fixed values of the X_i. Of course, the x_λ are fixed as well. In this interpretation $dF(\pi_i)$ is called the *likelihood function*. This term expresses the fact that this function is akin to probability, although we have no basis for speaking of the probability of a reservoir β, nor is dF normalized; indeed, $\int dF(\pi_i)\, d\pi_i$ need not exist.[19]

We proceed to maximize dF with respect to the π_i and define the estimated, or most likely, intensities as the particular values $\hat{\pi}_i$ for which the likelihood function becomes a maximum, given the set of measured values x_i. As we have seen, $dF(\pi_i)$ is an analytic function of the π_i ; thus, this maximization is achieved

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[19] Of course, a likelihood function can be defined for any d.f. Our problem is simplified because we have established the fact that the interaction between system and reservoir is governed by the canonical d.f. We note that this d.f. may have a direct physical meaning, for example, a system serving as a thermometer in prolonged contact with $R(\beta)$. If numerous energy measurements are performed, their average is the canonical average. Another possibility is, however, that the system acquired its energy by some other means than through contact with a reservoir $R(\beta)$. Thus macroscopic work might be dissipated in the system after thermal isolation had been established. In this case we proceed with the estimation of β exactly as described above, although the canonical ensemble will have only fictitious, "virtual" existence. An interesting case is a spin system exhibiting "negative temperatures" (*19*), which has been brought into this state by the reversal of a magnetic field. The negative temperature is that of a fictitious reservoir that could have brought the system into the same state by contact.

by differentiation. Since dF is positive for the set of x_i that are at all observable, we may maximize instead of dF its logarithm. We have

$$\ln dF(x_i\,,\,\pi_i) = \ln dG(x_i) - s(x_i\,,\,\pi_i)/k, \tag{4.1}$$

where

$$s(x_i\,,\,\pi_i)/k = \Phi(\pi_i) + \sum \pi_i x_i \tag{4.2}$$

is the random entropy function, or index of probability. For the sake of brevity, we suppress the fixed variables x_λ which, in fact, are present in the arguments of each term of (4.1). Evidently, maximizing $\ln dF$ with respect to the π_i at constant x_i is identical to minimizing $s(x_i\,,\,\pi_i)$ under the same conditions. Hence we have

$$\frac{1}{k}\frac{\partial}{\partial \pi_i}\,[s(x_i\,,\,\pi_i)]_{\pi_i=\hat{\pi}_i} = \left(\frac{\partial \Phi}{\partial \pi_i}\right)_{\pi_i=\hat{\pi}_i} + x_i = 0 \tag{4.3}$$

with the stipulation that the matrix with the elements

$$\frac{1}{k}\,\frac{\partial^2 s}{\partial \pi_i\,\partial \pi_k} = \frac{\partial^2 \Phi}{\partial \pi_i\,\partial \pi_k} = \Phi_{ik} \tag{4.4}$$

be positive semidefinite.

Equation (4.3) can be written

$$\bar{x}_i(\hat{\pi}_i) = x_i\,. \tag{4.5}$$

The most likely values of the intensities π_i are defined by the requirement that the empirically given values x_i be equal to the canonical averages conditioned by the π_i.[20] Condition (4.3) is of a form identical to (3.5) and always possesses a single set of positive solutions. The matrix (4.4) is identical to the matrix of covariances (3.6) and, accordingly, it is positive semidefinite. However, in the limiting case of absolute zero we have det $|\,\Phi_{ik}\,| = 0$. This means that the averages $\bar{x}_i(\pi_i)$ become insensitive to the variation of $\pi_1 = 1/kT$; and while the estimation of the $\bar{x}_i$ by x_i remains good, the inference with respect to π_i becomes, unreliable. This is the expression in our formalism of the well known difficulties of thermometry near absolute zero, which result from the flattening out of the temperature dependences of the thermometric indicators.

C. The Statistical Thermostatics of Isolated Systems

We shall now develop a thermostatic formalism for isolated systems that is formally similar to the canonical theory, but, instead of being based on the

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[20] Although this result is plausible, it is not trivial. Without the above analysis we might have required that x be equal to the most probable value of the d.f. conditioned by π_i . No useful formalism results from such a postulate.

conjugate pairs of fixed intensities π_i and average extensive quantities $\bar{x}_i$, is expressed in terms of fixed extensive quantities x_i and most likely intensities $\hat{\pi}_i$.

In this formalism the role of entropy is played by a function that we call the estimated entropy and define as

$$\begin{aligned}\hat{s}(x_i) &= \min_{\pi_i} \{s(x_i, \pi_i)\} \\ &= \min_{\pi_i} k\{\ln Z(\pi_i) + \sum \pi_i x_i\}.\end{aligned} \tag{4.6}$$

Comparison of (4.6) with (4.3) and (4.4) indicates that this minimum problem has indeed a unique solution for $\pi_i = \hat{\pi}_i$.

Comparing Eq. (4.6) with (3.9) we see that, while the canonical entropy $\bar{s}(\pi_i)$ is obtained from the random entropy $s(x_i, \pi_i)$ by averaging over the x_i at fixed π_i, the estimated entropy is obtained from the same function by minimization with respect to the π_i at constant x_i. Since the minimum is reached for $\pi_i = \hat{\pi}_i$, we can also write

$$(1/k)\hat{s}(x_i) = \Phi(\hat{\pi}_i) + \sum \hat{\pi}_i x_i. \tag{4.7}$$

From (4.7) and (3.9), we have

$$\bar{s}(\hat{\pi}_i) = \hat{s}(x_i). \tag{4.8}$$

We see from (4.8) that the variational principle (4.6) can be expressed formally for the canonical entropy as follows:

$$\bar{s}(\hat{\pi}_i) = \min_{\rho_i} k\{\Phi(\rho_i) + \sum \rho_i x_i\}, \tag{4.9}$$

where the minimum is taken with respect to the dummy variables ρ_i at constant x_i. The minimum is reached for $\rho_i = \hat{\pi}_i$, and the x_i are eliminated by means of (4.5). This useful variational principle is valid independently of the method of the maximum likelihood estimate and was, indeed, obtained by Fowler (*20*), and used extensively by Khinchin (*11*). In their interpretation, however, the extremum-principle lacks the intuitive meaning provided by the maximum-likelihood estimate in the formulation given in Eq. (4.6).

We show now that

$$\hat{s} = \hat{s}(x_i) \tag{4.10}$$

can be considered as the fundamental equation of the system (X) with all the properties postulated for such equations in MTE. We have from (4.7) and (4.3)

$$\frac{1}{k}\frac{\partial \hat{s}}{\partial x_i} = \hat{\pi}_i + \sum_k \frac{\partial \hat{\pi}_k}{\partial x_i}\left[x_k + \frac{\partial \Phi(\hat{\pi}_k)}{\partial \hat{\pi}_k}\right] = \hat{\pi}_i. \tag{4.11}$$

In particular, and defining $k\hat{T} = 1/\hat{\pi}_1$, we have for $x_1 = u$, $\pi_1 = 1/kT$,

$$dx_i = 0 \ (i \neq 1)$$
$$d\hat{s} = du/\hat{T}. \tag{4.12}$$

Since du is a heat quantity, we see that $\hat{s}$, $\hat{T}$ are indeed satisfactory conjugate variables with some of the main connotations of entropy and temperature.

We shall show now that the relation (4.5) implies the same maximum property for the entropy $\hat{s}$ that has been postulated in (*MTE*) (*P b1*) for the macroscopic entropy.[21]

Suppose that we have two isolated systems (x') and (x''). The estimated entropy of the composite system is

$$\begin{aligned} \frac{1}{k}(\hat{s}' + \hat{s}'') &= \min \{\Phi + \textstyle\sum \pi_i x_i\} \\ &= \min \{[\Phi' + \textstyle\sum \pi_i' x_i'] + [\Phi'' + \textstyle\sum \pi_i'' x_i'']\}, \end{aligned} \tag{4.13}$$

where $x_i' + x_i'' = x_i$. If the two systems are isolated and united only in a formal fashion, the two square brackets are to be minimized independently, and they reach their minima at $\hat{\pi}_i'$ and $\hat{\pi}_i''$, respectively. On the other hand, if the systems are coupled, they must have a common $\hat{\pi}_i$, with the x_i constant rather than the x_i' and x_i''. The restriction of the set of comparison states cannot decrease the minimum, hence

$$\hat{s} \geqq \hat{s}' + \hat{s}''. \tag{4.14}$$

The equality sign is valid only if $\hat{\pi}_i' = \hat{\pi}_i''$.

Relation (4.14) is valid also for the subdividing of a simple system by an adiabatic wall, an operation leading to an entropy that is less than or equal to the original value. A decrease of the entropy occurs if the subsystems are found with $\hat{\pi}_i' \neq \hat{\pi}_i''$. Hence we have to ask ourselves how these results are reconciled with the irreversible increase of entropy. The answer lies in the interplay of thermodynamic operations and processes. The former are manipulations of constraints, the latter are molecular processes that take place under the given set of constraints. The importance of this interplay for the description of composite temporal processes has been discussed elsewhere (*6*). Briefly, it is perfectly feasible, through a sequence of thermodynamic operations involving an expenditure of work, to prepare an initial state for which $\hat{\pi}_i'$ and $\hat{\pi}_i''$ of the isolated systems are considerably different from each other. In contrast, the probability of trapping the system by subdivision in a final state with values $\hat{\pi}_i'$ and $\hat{\pi}_i''$ is given by the microcanonical d.f. It is intuitively evident, and can be confirmed by the methods of Section V, that this probability decreases to negligible values if $\hat{\pi}_i'$ and $\hat{\pi}_i''$ are significantly different from each other.

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[21] This proof is a simple generalization of the one given by Khinchin (*11*, p. 138) based on relation (4.9).

Relation (4.14) is identical to the entropy maximum principle *P b1* of (MTE) and can serve as a point of departure for developing the entire formalism of MTE. This connection can be brought out also by rewriting relation (4.6) as

$$\hat{s}(x_i) \leqq k(\Phi + \sum \pi_i x_i), \tag{4.15}$$

where the equality sign is valid if and only if the π_i are the estimated intensities corresponding to the given x_i. We shall say that such pairs of x_i, $\hat{\pi}_i$ are *matched*. By using (3.13) we rewrite (4.15) in the energy scheme as

$$U - \hat{s}T - \sum{}' x_i P_i - U[T, P_i] \geqq 0. \tag{4.16}$$

Relation (4.16) is formally similar to (3.15) in the canonical formalism but, in contrast with the latter, the present relation can be identified with the extremum principle (5.20) of (MTE). The concept of "matching" system quantities and reservoir intensities has a meaning in MTE: the variables are matched in equilibrium. Therefore the comparison states in the variational principle (4.15) or (4.16) are the same as in MTE. In contrast, in the canonical formalism the comparison states are noncanonical distributions which cannot be interpreted in MTE.

D. Equilibrium, Objective Entropy, and Nernst's Law

Taking stock of the connection between thermodynamic theory and experiment, we find that, at the present stage of the discussion, the situation is still beset by a serious limitation. Among the central concepts of thermodynamics is that of *equilibrium*. Without this concept we could not even express the first law of thermodynamics in a meaningful fashion, inasmuch as we could not construct an energy function in terms of macroscopic variables only. Yet there is no purely operational method for distinguishing a state of thermodynamic equilibrium from a quiescent nonequilibrium state. Experiment allows us to determine the entropy difference between any two equilibrium states, provided that they can be connected by a quasi-static path. The requirement of consistency for different paths provides a *necessary* criterion that the actual paths are reasonably quasi-static. However, this criterion is not *sufficient*. This is particularly significant if the system has internal degrees of freedom, such as the orientation of molecular groups, or nuclear or electronic spins. A consistent value for the entropy difference may mean either that the hidden degrees of freedom are in equilibrium throughout, or that they are completely frozen. In order to decide which of these alternatives is relevant one must be able to integrate empirically between two states of known entropy. It is precisely the knowledge of the entropy in two reference states that is provided by a sufficiently sharp formulation of Nernst's law (*21*). The two reference states are those for which either the temperature or the density tends to zero. The first limiting case can be handled in STE only by the same postulational method as that in MTE.

Pc 2. The entropy of every thermodynamic system in equilibrium approaches, in the limit of vanishing temperature, $k \ln g_0$ where g_0, the degeneracy of the ground-state, is a small integer whose order of magnitude is independent of the size of the system.

We may add that this limit is reached sufficiently smoothly so that the entropy practically vanishes at attainable temperatures.

At the end of this section we shall make a few remarks about the microscopic meaning of this postulate. Meanwhile, we turn to the case of vanishing density. Practically every system subject to thermostatic study can be transformed into a nearly perfect-gas state. Under these conditions, the calculation of the entropy of the system is reduced to that of a molecule (see Section III, B), and the latter calculation can, in many cases, be performed from spectroscopic data.

The formalism of MTE and of STE is meaningful only when it is considered *relative* to the set of chemical reactions used to define the independent components (*C a3*) of (*MTE*).

In view of this situation, we have to compute the entropy in relation to various plausible assumptions concerning the relevant independent components. (Decisions have to be made concerning the inclusion of isotopic constitution, nuclear spin, and the like.) Once this choice has been made, the entropy has an absolute meaning in the sense that it depends only on the counting of quantum states without any arbitrary or conventional constants.[22] By integrating the experimental caloric data from this gaseous state to the vicinity of absolute zero, it is possible to decide whether the low-temperature system is in equilibrium with respect to the various intrinsic variables. The method involves more than a simple routine, and for details we have to refer to the literature. In the hands of experienced workers it has led to significant detailed insights concerning equilibrium with a measure of assurance which would have been inconceivable without the careful dovetailing of experimental and theoretical procedures (*21*).

It is apparent that the procedure described deals with a type (iii) experimental situation (Section IV, *A*). *P c1* is a *qualified prediction* that can be used to perform retrodictions concerning the extent of the equilibrium prevailing in the system. Most of the discussions of Nernst's law within the context of the principles of thermodynamics are obscured by the fact that they do not evaluate this law in terms of its actual use, but are concerned with the fact that it does not conform to the supposed norm of the laws of physics, not being expressed as an *unqualified* prediction. At any rate, the literature on the subject is full of

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[22] The fact that the entropy is in one sense *relative* and yet in another sense *absolute* offers the possibility of semantic confusion, which beclouds much of the discussion of the subject. Another misconception is the assumption that the *relativity* of the entropy concept makes it also *subjective*. While there is, of course, a subjective element in the use of entropy, inasmuch as we may choose to ignore detail, we certainly cannot increase the detail beyond counting quantum-mechanical pure states.

reformulations that propose to correct this alleged shortcoming. One of the best known versions claims that "it is impossible to reach absolute zero." We do not question the interest inherent in this statement, when considered as a corollary of *P c2*. However, this formulation cannot be taken as an adequate replacement of this postulate since unqualified predictions have no retrodictive power.

Finally, we make a short remark concerning the microscopic interpretation of *P c2*. Let us consider a composite system consisting of N cell divisions and make an attempt to describe this system in terms of the present theory, that is, by assuming statistical independence of the cells even for small cells and large values of N. Under the assumption that the lowest state of each cell is g-fold degenerate, the lowest possible value for the entropy is of the order of $Nk \ln g$. This is in contradiction with *P c2*, unless $g = 1$. It is indeed widely believed that such an assumption is the proper explanation for Nernst's law (*22*). However, this assumption is unwarranted. For instance, a system containing an odd number of electrons has at least a double spin degeneracy. Yet there is no breakdown of Nernst's law and the system becomes, say, ferromagnetic or antiferromagnetic. The responsibility for the difficulty is undoubtedly the breakdown of the statistical independence of the cells. If the cells are strongly correlated, the degree of degeneracy of the system of N cells need not be larger than that of a single cell. The entropy per unit cell is then $s_0 = (k \ln g)/N$, and this quantity tends to zero as N goes to infinity. Hence Nernst's law is satisfied even in the presence of degeneracy of the microcells.

E. THE MICROCANONICAL FORMALISM

Up to this point our whole discussion has centered around the coupling of a finite system with an infinite reservoir. Although the assumption of infinite environments is almost always a reasonable assumption, it is of obvious interest to consider the coupling of two or more finite systems with each other. The formalism governing this situation is already implicit in the theory as it has been developed thus far. The so-called microcanonical d.f. describing the distribution of the energy of a system carved out of a finite system is given by (2.17). We can easily generalize that expression for the distribution of any set of x_i :

$$d\mathfrak{F}(x_i' \mid x_i) = \frac{dG'(x_i')\, dG''(x_i'')}{dG(x_i)} . \tag{4.17}$$

The generalization to more than two subsystems is obvious. The rigorous computation of this function is cumbersome, since the structure function of composite systems is obtained from that of its parts by convolution, (2.18). This contrasts with the much more manageable product rule for the generating function $Z(\pi_i)$.

Evidently, the complementary system X'' can be made into a reservoir by means of the limiting process $X'' \to \infty$, $X' =$ constant. Accordingly, the microcanonical d.f. tends to the canonical d.f. $d\mathfrak{F}(x_i' \mid x_i) \to dF(x_i', \pi_i)$. Since the latter is easier to handle, the microcanonical d.f. should be used in the present theory only if there are special reasons for considering this formalism more adequate for the problem at hand.

Two problems of this sort have been treated in the literature. The first is the emission of neutrons by heavy nuclei, considered as an evaporation process (*23*). Emission of neutrons by an infinite extension of nuclear matter would correspond exactly to the thermodynamic problem to be treated by the grand canonical method (Section III). The "reservoir" of nuclear matter would remain unaffected by the loss of one or of any finite number of neutrons. In reality, the original nucleus is substantially different from the product nucleus, a circumstance which is, of course, allowed for in the microcanonical separation problem. A second problem in which the finite size of the reservoir is significant is the calculation of critical fluctuations. Here the finiteness of the reservoir is essential to ensure finite fluctuation (*24*).

In the literature the use of the microcanonical ensemble has a much greater prominence than the foregoing discussion would suggest. The reason for this is that in traditional statistical mechanics it is imperative to use isolated systems as a point of departure, since the use of Liouville's theorem depends on such a procedure. The aforementioned difficulties of the microcanonical method are solved or circumvented by means of simplifying assumptions that are not dictated by the nature of the problem. We shall discuss these asymptotic assumptions in the next section.

V. ASYMPTOTIC THEORIES

It is an important feature of STE that the canonical d.f. is derived for systems in equilibrium with infinite reservoirs. While this same point of view is taken in refs. *8*, *4*, and *5*, the most widespread approach in the literature is different: the point of departure is a large but finite isolated system. In this microcanonical theory, the canonical d.f. is established approximately for a small subsystem of the isolated system. This subsystem is the system of interest; the complementary system plays the role of the reservoir. According to our results, of course, the canonical d.f. is not rigorously correct in this situation but only in the asymptotic case for which the complementary system tends to infinity.

Our first problem in this section is to establish asymptotic relations that are valid for large, but still finite, complementary systems. This is easily achieved in the present context, since we have the entire canonical formalism at our disposal, this formalism having been established without the asymptotic assumptions that are under scrutiny. The situation was much more complicated in the historical context in which the asymptotic methods were used to establish the canonical d.f. The complications produced by the finite size of the complementary system were solved either by means of conceptual oversimplifications or at the expense of formal complications and unduly restrictive conditions of validity. We shall attempt to clarify the nature of these conceptual oversimplifications, which have been severely criticized (see refs. *20, 11, 11a, 4*) but are still quite widely used.

We start by establishing an approximate expression for the structure function that plays a central role in the microcanonical theory.[23] For the sake of simplicity, we confine ourselves to canonical d.f.'s with a single random variable, the energy. By using (2.12) and (2.35) we obtain

$$\ln dG(u) = s(u, \beta)/k + \ln dF(u \mid \beta), \tag{5.1}$$

where β is considered as a fixed numerical parameter. Since the probability dF is smaller than unity, we have

$$k \ln dG(u) < s(u, \beta). \tag{5.2}$$

The interesting aspect of these relations is that by choosing appropriate values for u and du one can guarantee that $dF(u \mid \beta) \approx 1$. If this condition is satisfied, the last term in (5.1) becomes negligible and the inequality (5.2) turns into an approximate equality. To render this idea more quantitative, we approximate the canonical d.f. by a Gaussian d.f., the parameters of which are such that the energy and its variance have their correct canonical values:

$$dF(u \mid \beta) \approx \frac{du}{\sqrt{2\pi}\sigma} e^{-(u-\bar{u})^2/2\sigma^2}, \tag{5.3}$$

where

$$\sigma^2 = \text{Var}\,(u) = \overline{(\Delta u)^2}. \tag{5.4}$$

Since moments higher than the second are hardly ever important, the approximation (5.3) is expected to be satisfactory, at least in the neighborhood of the peak of the d.f.[24]

Inserting (5.3) into (5.1), we obtain, for $u = \bar{u}$,

$$\ln dG(\bar{u}) \approx s(\bar{u})/k + \ln du/\sqrt{2\pi}\sigma, \tag{5.5}$$

where $dG(\bar{u})$ is the number of quantum states between $\bar{u}$ and $\bar{u} + du$. (As usual, β in $s(u, \beta)$ can be expressed in terms of $\bar{u}$.) We define the function

$$\bar{s}(u) \equiv k \ln dG(u), \tag{5.6}$$

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[23] The idea of this approximation is found in Khinchin (*11*), although our interpretations differ, as we shall see at the end of this section.

[24] The Gaussian d.f. is justified also by the central limit theorem (*11*) whenever the system consists of many statistically independent parts.

and obtain in excellent approximation

$$\bar{s}(\bar{u}) = s(\bar{u}). \tag{5.7}$$

Equation (5.7) holds either if we put

$$du = \sqrt{2\pi}\,\sigma \tag{5.8}$$

or if we go to the limit of many degrees of freedom, $\mathfrak{N} \rightarrow \infty$ while keeping du constant. Since $\bar{u}$, $s(\bar{u})$ and σ are all proportional to $\mathfrak{N}$, we have

$$\bar{s}(\bar{u}) = s(\bar{u})[1 + O(\ln \mathfrak{N}/\mathfrak{N})]. \tag{5.9}$$

The function $\bar{s}(u)$, defined in Eq. (5.6), is the well known Boltzmann entropy.[25]

Following Boltzmann, the identification of $\bar{s}$ with the entropy of the system is usually justified in terms of the relation

$$dG'(u')\,dG''(u'') = dG(u) \tag{5.10}$$

where $u = u' + u''$ is the energy of the composite system. However, (5.10) is correct only for isolated systems and, in the case of coupling, we have to use either (2.17) or (2.18) instead. Thus, for coupled systems, $\bar{s}(u)$ does not have the additivity properties of the entropy. To be sure, the effects of this discrepancy are numerically negligible whenever relation (5.7) holds. Nevertheless, this discrepancy is a symptom of a conceptually unsatisfactory situation.

The definition of the canonical entropy given in Section II involves a sequence of well structured mathematical operations which we can represent symbolically as follows:

$$dG \rightarrow \Phi \rightarrow dF \rightarrow \bar{s}(\beta) \rightarrow \bar{s}(\bar{u}). \tag{5.11}$$

Or, formally, by using (2.30), we have

$$\bar{s}(\beta) = -k\beta^2 \frac{\partial}{\partial\beta}\left[\frac{1}{\beta} \ln \int_u e^{-\beta u}\, dG(u)\right] \tag{5.12}$$

and, finally, β is expressed in terms of $\bar{u}$ by inverting the relation

$$\bar{u} = -\frac{\partial}{\partial\beta}\left[\ln \int e^{-\beta u}\, dG(u)\right]. \tag{5.13}$$

These expressions mean that the Legendre transform of the logarithm of the Laplace transform leads us back, in virtue of (5.6) and (5.9), very nearly to the logarithm of the original starting point $dG(u)$. In spite of this fact, the telescoping

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[25] The entropy definition (5.6) has been used by both Boltzmann and Gibbs. Yet it has a place in the "neo-Gibbsian" theory of Sections I–IV only in the peripheral microcanonical formalism (IV,E), though it plays a central role in the theories of Boltzmann (*2*) and Einstein (*1*).

of the sequence of operations symbolized in (5.11) leads to an unwarranted fusion of the concepts of "structure function," "probability," and the exponential of the "entropy." Thus the structure function $dG(u)$ is usually called the "thermodynamic probability" of the system; and the entropy, the logarithm of this probability.

Actually, dG is not a probability, nor can it be normalized in any obvious way. In principle, the function $G(u)$ is obtained from the time-independent Schrödinger equation and does not have a statistical character, although in practice it is often computed by approximate statistical methods. Likewise, it is preferable not to call $e^{s/k}$ a probability but, rather, to associate microstates with probabilities and macrostates with d.f.'s; the entropy is a functional of these d.f.'s. A theory built upon the aforementioned identifications of concepts appears from the point of view of STE as a conceptually degenerate system, although, from the point of view of historical evolution, one should rather speak of a conceptually undifferentiated theory.

We may avail ourselves of relations (5.5)–(5.9) without any conceptual ambiguity wherever the situation warrants the use of such asymptotic relations. Thus we obtain a connection between entropy and probability by inserting (5.6) into (2.17):

$$d\mathfrak{F} = \exp \{[\tilde{s}'(u') + \tilde{s}''(u'') - \tilde{s}(u)]/k\}. \tag{5.14}$$

If we insert into this relation the quantity $s(\bar{u})$ from (5.5), we have the point of departure of Einstein's fluctuation theory (*1*).[26]

It is instructive to rewrite the canonical d.f. by using (5.1), (5.6), and (2.33):

$$\begin{aligned} dF(u \mid \beta) &= \exp [\{\bar{s}(u) - s(u,\beta)\}/k] = \exp [\tilde{s}(u)/k - \Phi(\beta) - \beta u] \\ &= \exp [\beta(\bar{u} - u) - \{\bar{s}(\bar{u}) - \tilde{s}(u) - \}/k] \qquad (5.15) \\ &= \exp [\{A(T) - (u - T\tilde{s})\}/kT]. \end{aligned}$$

Each of these expressions implies an inequality based upon the relation $dF \leqq 1$. Thus,

$$\tilde{s}(u)/k - \beta u - \Phi(\beta) \leqq 0 \tag{5.16a}$$

$$u(\tilde{s}) - T\tilde{s} - A(T) \geqq 0 \tag{5.16b}$$

where the equality sign is valid only if $dF = 1$. This relation, of course, cannot

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[26] It has been argued by Greene and Callen (*25*) that Einstein's fluctuation theory is rigorously equivalent to the canonical formalism. Their argument is inconclusive, since it hinges on the statement that "there is no distinct isothermal and adiabatic thermodynamics." This is true in MTE, but in STE it does not have even a precise meaning. The same functional form for the entropy function describes an isolated system in terms of $\hat{s}(u)$ and a diathermally coupled system in terms of $\bar{s}(\bar{u})$, provided that we use the formalisms of Sections IV and II of the present paper. However, the functional form of $\tilde{s}\ (u)$ is only asymptotically equal to the functions just considered. This is not good enough for the argument of Greene and Callen, who do not neglect the higher powers of Boltzmann's constant. This criticism does not affect their elegant formalism for the computation of fluctuation moments.

be exact. However, it is valid to an excellent approximation if the conjugate variables u and β(or $\bar{s}$ and T) are matched with each other, that is, if they are associated with a system and a reservoir which would be in equilibrium with each other according to MTE.

It is worthwhile to add a remark concerning the width du associated with the d.f. dF. The latter approaches unity for matched variables only if du is at least of the order of the standard deviation of dF. If the width of the d.f. is set to be much sharper, dF may become much smaller than unity. Yet, for macroscopic systems, the equality sign in (5.16) is still reached to a very good approximation. The excess over zero of the left-hand side is of the order of $k \ln \mathfrak{N}$, which is to be compared with the order of $k\mathfrak{N}$ in the case of nonmatching variables. This is again an instance of the insensitivity of the functions of MTE to statistical assumptions.

Consequently for matching variables, relation (5.7) is valid and $\bar{s} = s(\bar{u})$ becomes identical to the entropy of MTE. In contrast to the superficially similar inequality (2.41), the relation (5.16b) is identical with the extremum principle (5.20) of (*MTE*). The statistical interpretation is particularly simple for (5.16a), that is, in the entropy scheme rather than in the energy scheme: for a reservoir of given β, the matching energy is that of maximum probability (most probable energy). For given energy, the matching β is that obtained from the maximization of likelihood.

We shall discuss now somewhat more closely the approximate handling of the microcanonical distributions. Let us consider the partition of the energy u of an isolated system between two subsystems. The probability $d\mathfrak{F}(u' \mid u)$ of a particular division $u' + u'' = u$ is given by Eq. (2.17). The approximate procedure is to select those values u_0', u_0'' for which the probability is maximum.[27] It is apparent from the above discussion and, in particular, from (5.9) and (5.14) that the probability $d\mathfrak{F}$ can be made practically unity for the correct value of the energy and of the width of the distribution. The correct choice of the energy is the main part of the procedure and is sufficiently obvious. However, the proper choice of the width du' of the distribution, i.e., according to (5.8), is usually achieved in a rather hidden form by omitting the last term in the Stirling approximation

$$\ln N! \approx N \ln (N/e) + \tfrac{1}{2} \ln (2\pi N). \tag{5.17}$$

[27] This is usually expressed by saying that the distribution is "the most probable" one. There are several difficulties with this expression. It was pointed out by T. A. Ehrenfest (*26*) that there is no reason to expect that only the most probable values of a random variable should be observed. Moreover, we are justified in speaking of the probability of microstates, but the probability of a d.f. has no obvious meaning. However, as Mandelbrot points out (*4*), we may rationalize the traditional procedure by speaking of the maximization of $d\mathfrak{F}$ considered as "likelihood" (see Section IV). The maximization is carried out by means of Lagrange multipliers. These are the parameters estimated by the procedure.

The effect of this term is negligible if N is very large. This term is neglected, however, also under conditions in which the distribution is over many microstates and N is quite small. If this term were kept, the method of the most probable distributions would lead to wrong results; the probability of the most probable state, taken in an exact sense, would be much smaller than one. Thus, the use of the most probable distributions and the truncation of the Stirling formula are compensating mistakes. That the compensation is as perfect as it is seems fortuitous and, also, unfortunate, inasmuch as it has encouraged conceptually unsound practices.

We conclude this section with a short discussion of the work of Khinchin (*11*, *11a*), which occupies a special position among the theories that derive the canonical d.f. from the microcanonical d.f. This theory is conceptually correct; it was Khinchin, in fact, who introduced the concept of the structure function and contributed considerably to the clarification of the situation brought about by the degeneracy of the asymptotic theories. However, Khinchin's idea is that the mathematical basis of statistical mechanics is the central limit theorem (*11*); in the case of quantum statistics sharper limit theorems are used (*11a*). Physically, this means that Khinchin assumes that even the "small" subsystem consists of a large number of statistically independent parts. The use of this assumption, necessary in a rigorously mechanical theory, leads to considerable formal complications. On the other hand, in STE there is no need to use either this assumption or the corresponding limit theorems. One should compare, consequently, the simple and rigorous derivation of the quantum distribution laws in Section III, B with Khinchin's complicated approximate derivation (*11a*). Moreover, the door is left open in STE for further microscopic extensions of the theory.

VI. DISCUSSION

The canonical formalism developed in STE seems not unlike the one used in statistical mechanics. Nevertheless, the thermodynamic interpretation has aspects without a mechanical analog. A case in point is the theory of measurement of Section IV. In this theory the distinction between free and fixed variables plays an important role. The same distinction has also some bearing on the ergodic problem[28] and on the relation of entropy and information.

We have noted in Section I that our statistical postulates imply an ergodic property. We state now somewhat more precisely that this property is identical to that of the mathematical ergodic theorem (*11*). Curiously, in the literature this theorem is considered to be either insufficient or irrelevant for the purposes

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[28] Unfortunately, the term "ergodic" is used to mean many things. It is not within the scope of this paper to deal with this question either with great precision or from many different angles. We shall outline only the particular point to the clarification of which we hope to contribute.

of statistical physics. In the texts of statistical mechanics the ergodic hypothesis is usually formulated in essence as follows: the time average of a phase function of a dynamical system is equal to the average of the function taken over the *entire* energy surface. This is attributed to the underlying dynamics according to which the phase point representing the system covers the energy surface sufficiently densely. This statement implies that, except for the volume and the number of invariant particles, the only fixed variable of the system is the energy. We shall call this the "strong" form of the ergodic hypothesis.

The mathematical ergodic theorem is a weaker statement, inasmuch as the proof is subject to the condition that the system be metrically transitive or, equivalently, that its phase space be metrically indecomposable. This restriction guards against the possibility that the system might be trapped in one of several domains of the energy surface which are invariant under the transformation representing the dynamical law. If such domains exist, the averaging is to be performed only over the domain in which the system happens to be trapped. This state of affairs is quite in keeping with the phenomenological situation described in STE. Since we have not committed ourselves in advance concerning the full listing of the fixed variables, we can introduce an appropriate set to be associated with each domain.

The diversity of situations that may arise can be illustrated by two typical examples. There are realizable experimental conditions in which the number of ortho- and para-hydrogen molecules are separately conserved. The methods of STE are still applicable provided that additional fixed variables are admitted. Another case is furnished by a system such as glass. Here we have a huge number of fixed variables distributed at random which cannot be explicitly managed; and the methods of STE do not strictly apply. We have a frozen-in nonequilibrium, also called a false equilibrium.

Since the tendency to form stable configurations is a basic property of matter, we cannot hope to provide a proof of the strong version of the ergodic hypothesis, because that would be contrary to fact. Of course, it is legitimate to explore the problem of the validity of the strong ergodic hypothesis for special systems consisting of inert particles. However, this problem is of no basic importance for STE.

The distinction between free and fixed variables allows us to throw some light on the interpretation of expression (2.37). This expression for the entropy conveys, as well, the notion of statistical uncertainty; it arises also as a quantitative measure of information (*5a*). Accordingly, there have been many suggestions that entropy be considered as a measure of subjective ignorance and that information be related to negative entropy. Although there is undoubtedly some value in these suggestions, the conceptual unification they tend towards is bought at the price of losing important shades of meaning.

To avoid this difficulty, we propose the introduction of a generic term, designating (2.36) or (2.37), with $k = 1$, as the *dispersal of the distribution*. Of course, this term is to be distinguished from the *dispersion of a random variable*, a synonym for its variance or relative quadratic moment. Thus in a uniform distribution over g degenerate states the dispersion of the energy vanishes whereas the dispersal of the distribution is $\ln g$.

We consider now three typical situations in which the dispersal of the d.f. assumes the character of entropy, information, and uncertainty, respectively. However, these cases are by no means exhaustive. In particular, the concept of information has many ramifications which are outside the scope of the present discussion.

(i) The first case is that of an ergodic system in thermodynamic equilibrium, identified by invariant fixed variables. The system makes incessant transitions among states specified by free variables. The entropy is the dispersal of the d.f. over these transient states. The fact that we calculate the properties of the system by averaging over the free variables is not because of our *ignorance*, but because we *know* that the system actually exhibits a behavior that is the average of that of the transient states. The microscopic dynamics responsible for these transitions and, hence, for ergodicity, brings about the adjustment of the system to new external conditions, a prerequisite for the possibility of extracting the maximum amount of work out of it. Thus ergodicity is a prerequisite for the entropy's having the standard thermodynamic meaning.

(ii) We consider now a distribution of molecules that belong to a finite number of classes that are isomers or other well defined variants of each other. In polymer chemistry one speaks of poly-dispersivity. The situation is described in terms of d.f.'s which, in our terminology, are taken over the fixed variables that distinguish the above mentioned classes. These d.f.'s are nonergodic and their dispersal provides a numerical measure of poly-dispersivity.

In the case of genetic material the "poly-dispersivity" of the DNA molecule stores genetic information. If a subensemble of molecules is selected, that are all in identical configurations described by the same set of fixed variables (a "pure strain"), the dispersal of the new d.f. is zero. The difference between the dispersals of the original d.f. and the new one is taken as the measure of information stored up by the selection of the subensemble.

Of course, the macromolecules partake also in thermal agitation (internal vibration and rotation). The dispersal of the d.f. over these states is their entropy, an entirely different quantity. The present point of view also disposes of the difficulties that arise if negative entropy is taken as a measure of the degree of organization. The paradoxical character of this alleged connection has been demonstrated in terms of a simple numerical example by Klein (*27*).

(iii) Systems in false equilibrium, such as a glass, are characterized by a huge number of quasi-fixed variables distributed at random. These variables are practically constant compared, say, with the free variables specifying the phonon states. Nevertheless they are subject to a slow drift.

The dispersal of the free-variable distribution could be used as an entropy. However the usefulness of this quantity is impaired by the fact that we cannot precisely identify the system to which it belongs. It is possible, in principle, to consider a virtual ensemble of glasses described by a d.f. over the quasi-fixed variables distributed at random over a continuum. The dispersal of this d.f. would be, indeed, a measure of our ignorance. The usefulness of this quantity has not yet been demonstrated, however, and we bring up the case only as a contrast with cases (i) and (ii).

We conclude with a few remarks concerning the relation of STE to MTE. Evidently, the former reduces to the latter as Boltzmann's constant tends to zero. Using a terminology introduced before (*6*), STE is "dominant" to MTE. An interesting aspect of this relation is that the fundamental equation of MTE remains valid in STE and has even the same functional form. The difference is in the conceptual interpretation of the conjugate couples of variables, X and π, of MTE. In STE there are two alternative interpretations: we have either $\bar{x}$ and π, that is, the actual intensities of reservoirs and averages of the additive invariants of systems, or x and $\hat{\pi}$, fixed values of the invariants coupled with estimated reservoir intensities. The transition to MTE means that these two interpretations coalesce.

In view of this situation the following possibility arises for the presentation of MTE. Instead of introducing the entropy postulationally as an undefined concept, as was done in Section I, B of (*MTE*), we could start, with some adjustments, from the present postulational basis and develop in this fashion the entire material contained in (*MTE*). We do not propose actually to do this, however, since we believe that STE is no more than a stepping stone toward another dominant theory that should be an even more satisfactory starting point for the structuring of thermodynamics. In such a future theory, correlations and time-dependent processes and operations should be handled explicitly. There is, of course, an extensive literature devoted to these problems. It seems however, that these always involve procedures that are, in one way or another, analogous to the asymptotic procedures discussed in Section V. The development of a theory that can be considered as a generalization of the formalism contained in Sections I–IV still has major difficulties to overcome.

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