

On the Derivation of Statistical Thermodynamics from Purely Phenomenological Principles

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Szilard pointed out in 1925 that it is possible to base the foundations of statistical thermodynamics upon "phenomenological" principles, analogous to those of the non-statistical "classical" theory. This approach is discussed and developed.

1. INTRODUCTION

THERE is a widespread belief among physicists that statistical thermodynamics cannot be derived from "phenomenological" principles relative to macroscopic experiments, however idealized. Actually, in an admirable paper, Leo Szilard¹ has shown the two aspects to be quite compatible. Unfortunately, the paper is difficult, complicated and even confusing, and is unduly pessimistic about its own scope. But its general idea should be revived and further developed. Moreover, while Szilard's mathematical and conceptual framework is quite isolated within physics, we have earlier shown² that it leads itself readily to the introduction of certain powerful methods of probability theory and mathematical statistics as yet unexploited in

thermodynamics. (Refs. 1 and 2 have been utilized in a recent treatment of the statistical thermodynamics of equilibrium³). The present paper will summarize² and will discuss several problems related to the place within phenomenological statistical thermodynamics of the second principle and of several alternative concepts of entropy.

It will be noted that, since a part of the laws of statistical mechanics can be obtained without any mechanical consideration, the term "statistical thermodynamics" will be used to designate the results of the statistical theory, without implying anything about the method used to derive them.

We insist, with the classical thermodynamicists, on a strict separation between the results linked to the zeroth and first principles, and those also requiring the second. For example, our zeroth principle differs sufficiently from that of Szilard to make the second principle unnecessary in order

¹ L. Szilard, *Z. Physik* **32**, 753 (1925). Do not confuse this reference with *Z. Physik*, **53**, 840 (1929).

² B. Mandelbrot, *Ann. Math. Stat.* **33**, 1021 (1962). For an early announcement of this result, see *Compt. Rend.* **243**, 1835 (1956).

³ L. Tisza and P. M. Quay, *Ann. Physics* **25**, 48 (1963).

to derive Gibbs' canonical distribution, and the concept of qualitative temperature.

Being parallel to statistical mechanics and thermodynamics, our method stresses more than is usual the parallelism existing between the two classical approaches. As a matter of fact, we shall stress the following: from the viewpoint of statistical mechanics, the physical statements upon which it is based may be considered as being "principles", and it happens that they can be associated one-to-one with the classical "principles" of phenomenological thermodynamics.

The random variable "energy" is designated by U and Gibbs' canonical distribution—as applied to isolated states—is written as

$$\exp(-\beta u)/Z(\beta).$$

However, from our purely phenomenological viewpoint, there is no sense in considering the states themselves; we rather have to consider surfaces of given energy, or sets made up of a number of such surfaces. As a result, we need a less precise form of the canonical law. Let us write $F(u | \beta)$ for the probability that the system be found in a state of energy equal to u or smaller. Then, designating by $G(u)$ the equivalent of the number of states of energy equal to u or smaller, we write Gibbs' distribution as follows:

$$dF(u | \beta) = d[\text{Pr}(U \leq u)] = dG(u) \exp(-\beta u)/Z(\beta).$$

This law plays the central role in our considerations. It is more than a convenient auxiliary mathematical device.

We shall need to repeat certain well-known arguments, in order to insert them within our development; we hope that these repetitions will not be too bothersome.

2. DERIVATION OF GIBBS' CANONICAL DISTRIBUTION FROM "ZEROTH" AND "FIRST" PRINCIPLES: TERMINOLOGICAL COMMENTS UPON THE STATISTICAL-MECHANICAL APPROACH

It is well known that Gibbs' law can be obtained, as an asymptotic approximation, from the distribution of a small part of a large physical system. The latter distribution is itself deduced from the following assumptions:

(0) A system known to have an energy U contained between u and $u + du$ can be found with equal probabilities in either of $dG(u)$ "states", where $G(u)$ is a nondecreasing function of u .

(1a) Energy is the unique invariant of certain physical transformations, those resulting from "thermal interaction".

(1b) When thermal interactions are weak, the energy is an additive expression.

(1a) and (1b) have an obvious connection with the "first principle of thermodynamics" and (0) serves to first introduce the concept of temperature, and can therefore be associated with the "zeroth principle". That is, even if one succeeds in deriving this principle from mechanics by some "ergodic" argument, such a derivation would be foreign to thermodynamics; from the viewpoint of that science, (0), (1a) and (1b) should rather be considered as "principles". The only purpose of the present section is to recommend such a nomenclature.

3. DERIVATION OF GIBBS' CANONICAL DISTRIBUTION FROM A "ZEROTH" AND A "FIRST" PRINCIPLE: A PURELY PHENOMENOLOGICAL APPROACH

Let us now summarize the results of our previous paper.² Its purpose is to show that, the zeroth and first principles can be rephrased so as to remain fully "phenomenological", while permitting a derivation of the canonical distribution, without any mechanical interpretation of $G(u)$.

The concept of a representative space, or "A-space".

By definition, the set of all possible outcomes of all the macroscopic measurements performed upon a system will constitute an "A-space" for that system. It will depend upon the physical structures of both the system and its environment and will not require or provide any microscopic mechanical substratum.

A stochastic concept of thermal equilibrium.

We assume that, when a system is in thermal equilibrium with its environment, the position of the corresponding "A-point" is random.

Conditioning.

A physical conditioning is any set of operations, which can be realized by purely macroscopic physical operations, and which impose some mathematical relation upon the A-point of a physical system.

For example, let the system S be made up of M parts S_m , and let the combinations of the energies U_m of these parts be the only macroscopically measurable characteristics of S . If S is in contact with an infinite environment, its A-point, of coordinates U_m , is any point of the positive hyper-quadrant of M -dimensional Euclidean space. If the environment is finite and of total energy u , the A-space is the domain in which all $U_m \geq 0$

and $\sum U_m \leq u$. If S is "isolated", the A -space is the domain in which all $U_m \geq 0$ and $\sum U_m = u$.

The physical content of our "zeroth principle".

When appropriate mathematical restrictions are imposed upon the A -space and upon conditioning relations, the following two paragraphs will express a physical principle that can be referred to as being the "zeroth", although its relation with the statement that usually goes under this name may only transpire gradually.

The nature of "thermal equilibrium" is such that when a system is in equilibrium under a condition R' , more stringent than an earlier condition R'' , the distribution of the A -point no longer depends upon the parameters that have characterized R'' .

Moreover, the equilibrium distribution under the physical condition R' may be obtained as follows: begin by the distribution relative to any less-strict condition R'' , consider R' as being a mathematical relation and apply the rules of probability theory relative to conditioning.

We may consider this statement of the zeroth principle as referring to a kind of equilibrium between a system and its parts.

The first principle.

We shall express the first principle by the *unicity* portion of the statement made in Sec. 2. The *additivity* portion of that statement will rather be replaced by the following statement.

The auxiliary principle of the existence of heat reservoirs.

There exists a family of physical systems, to be called the "heat-reservoirs", which can simultaneously serve as environments for several distinct systems S_m , and are such that the corresponding phase points are statistically independent random variables.

Derivation of the canonical law.

It was shown in Ref. 2 that the canonical law can be derived from the combination of the zeroth, first, and auxiliary principle, with the help of certain known theorems.

Reference to statistical sufficiency.

The preceding statements are somewhat isolated in the context of physics, but they happen to be intimately related to a branch of mathematical statistics, called the theory of sufficiency. For technical details, we must refer to the textbooks

of statistics,⁴ but we may say that a probability distribution is said to possess a sufficient statistic if the following is true: Suppose that one wants to "estimate" β from a sample of M values u_m of U ; this means that, given a finite sample, one wants to "guess" reasonably the value of the parameter of an infinite population from which the sample has been drawn. It is obvious that such guessing cannot be performed without some ambiguity and that even the best-trained people may disagree about the best method of estimation. Therefore, if one does not want to prejudice the statistician's procedure, it is in general necessary to furnish him with the complete collection of values of u_m . This is of course unwieldy, so that data collectors are very pleased when—irrespective of their statistician's preferences—the data can be summarized exhaustively and without loss by giving a small number of functions $R_i(u_1, \dots, u_M)$. For example, if the parent population is Gaussian, the set of u_m can with no loss be summarized by $\sum u_m$ and $\sum (u_m)^2$. Such a set of numbers R_i is what is called a "sufficient statistic".

Clearly, such a set of functions exists if, and only if, the probability distribution of the random variables U_m , given the R_i , is independent of the value of the parameter β . This has a close counterpart in physics; indeed, the joint distribution of the energies of M systems, given their total energy, is known to be independent of the temperature of the heat reservoir with which the M systems used to be in contact. The purpose of our previous paper² was to exploit this general idea more fully and more rigorously, in particular in deriving the canonical distribution.

4. DERIVATION OF THE CONCEPT OF ENTROPY FROM A "SECOND PRINCIPLE": THE STATISTICAL-MECHANICAL APPROACH

This section purports to stress a conceptual viewpoint that completes that of Sec. 2, and to suggest the corresponding terminology. Once the canonical law has been derived, and the concept of heat has been introduced, it is well known that the path-integral of the expression " $\oint \beta dQ$ " can be written as:

$$\Delta[\beta E(U)] - \oint \left\{ (\partial/\partial\beta) \log Z(\beta, \bar{V}) d\beta - \beta \sum \left[\int dF(u | \beta, \bar{V}) (\partial u/\partial V_k) \right] dV_k \right\},$$

⁴ C. R. Rao, *Advanced Statistical Methods in Biometric Research*, (John Wiley & Sons, Inc., New York, 1952). R. B. Hoag and A. T. Craig, *Introduction to Mathematical Statistics* (The Macmillan Company, New York, 1959).

where \bar{V} , of coordinates V_k , is the vector of external parameters of the system, and $(\partial u / \partial V_k)$ is the "adiabatic change" of the energy of a system when the external parameter V_k is varied alone (in Sec. 7, we shall return to this concept).

For this " $\oint \beta dQ$ " to be path-independent, it is sufficient that the following be true:

$$(*) \quad -\beta \int dF(u | \beta, \bar{V}) (\partial u / \partial V_k) \\ = (\partial / \partial V_k) \log Z(\beta, \bar{V}).$$

If this is indeed the case, one can write

$$\oint \beta dQ = h_{\text{final state}} - h_{\text{initial state}},$$

where h is the entropy, defined as

$$h = \beta E(U) + \log Z(\beta, V).$$

In turn, condition (*) is satisfied if $G(u)$ satisfies the condition of "adiabatic invariance". This statement, seldom as much emphasized as in the writings of Paul Ehrenfest,⁵ can of course be proven from mechanics. However, we think that—from the viewpoint of thermodynamics—it should rather be considered as being a basic "principle", namely the "second principle of statistical mechanics". (It is in fact somewhat surprising that, in view of the popularity of "conservation principles," the present one should have been discussed so little.) The simplest case is that of nondegenerately quantized energy, where $G(u)$ varies only for a denumerable number of values u_i of energy, and where $dG(u_i) = 1$ for all i . Let us recall that adiabatic invariance means that every energy level is a function of V over the same range of values of \bar{V} ; no energy level is either created or annihilated by a change of volume. More generally, the function $G(u)$ is defined only up to multiplication by an arbitrary function of \bar{V} (which vanishes from the distribution of u); this multiplier must be susceptible of being chosen in such a fashion that, when u^+ and u^- perform a free adiabatic transformation, $G(u^+) - G(u^-)$ remains invariant.

The above classical result has an important, but less well known, classical partial converse: Ehrenfest (Ref. 5, p. 347) has indeed shown that, in order that $\oint \beta dQ$ be path-independent and equal to Δh , adiabatic invariance is not only sufficient but also necessary.

5. DERIVATION OF THE CONCEPT OF ENTROPY—AND OF ADIABATIC INVARIANCE—FROM THE USUAL SECOND PRINCIPLE OF THERMODYNAMICS

Of course, adiabatic invariance could also be added to the zeroth and first principles, as stated in Sec. 3. However, it would have little meaning because $G(u)$ has no mechanical interpretation there. It is therefore fortunate that our zeroth and first principles can be continued by any of the classical forms of the phenomenological second principle.

For example, we can postulate directly that the Pfaffian form dQ has an integrating multiplier B . This quantity cannot be a function of the external parameters, and can therefore only be a function of the "qualitative temperature" $1/\beta$ introduced by Gibbs' canonical law. [Or else, the existence of the multiplier B can be deduced from Carathéodory's principle, as applied to the mean values of the random variables in question: "in the neighborhood of any mean state of a system (as defined by β and by \bar{V}) there exist states that cannot be reached—on the average—by any transformation in which the initial and final state of the environment are identical."]

Let us now show that adiabatic invariance is a necessary consequence of the fact that the integrating multiplier of dQ is a function $B(\beta)$; and, moreover, that this integrating multiplier must be β itself. This result will of course be stronger than Ehrenfest's classical statement referred to in Sec. 4, because we shall not require a priori that β itself be the integrating multiplier, and we shall not require that the integral be equal to the variation of h , as defined classically.

The smooth case.

First suppose that all the quantities of interest are continuous and derivable as often as required. Then, if the integrating multiplier is independent of \bar{V} , the following must hold for every couple of parameters V' and V'' :

$$\frac{\partial}{\partial V''} \frac{\int \frac{\partial u}{\partial V'} G'(u) e^{-\beta u} du}{\int G'(u) e^{-\beta u} du} = \frac{\partial}{\partial V'} \frac{\int \frac{\partial u}{\partial V''} G'(u) e^{-\beta u} du}{\int G'(u) e^{-\beta u} du}.$$

This in turn leads to the requirement that

$$\frac{\int \frac{\partial u}{\partial V'} \frac{\partial G'}{\partial V''} e^{-\beta u} du}{\int G' e^{-\beta u} du} = \frac{\int \frac{\partial u}{\partial V''} G' e^{-\beta u} du}{\int G' e^{-\beta u} du}$$

⁵ P. Ehrenfest, *Collected Scientific Papers* (Interscience Publishers, Inc., New York, 1959).

$$\frac{\int \frac{\partial G'}{\partial V''} e^{-\beta u} du}{\int G' e^{-\beta u} du} = \frac{\int \frac{\partial u}{\partial V''} \frac{\partial G'}{\partial V'} e^{-\beta u} du}{\int G' e^{-\beta u} du} - \frac{\int \frac{\partial u}{\partial V''} G' e^{-\beta u} du}{\int G' e^{-\beta u} du} \cdot \frac{\int \frac{\partial G'}{\partial V'} e^{-\beta u} du}{\int G' e^{-\beta u} du}. \quad (1)$$

Every term of this identity is the canonical average of some function $f(u)$; if the systems are very large, one can write:

$$\frac{\int f(u) G' e^{-\beta u} du}{\int G' e^{-\beta u} du} \sim f[E(U)] + \frac{1}{2} f''[E(U)] D,$$

where D is the variance of U . Naturally, in order that (1) be satisfied, it is necessary (and we shall see that it is also sufficient) that it be satisfied up to terms of second order, for every value of $E(U)$, i.e., of β . This yields the requirement

$$\frac{\partial}{\partial u} \left[\frac{\partial \log G'}{\partial V''} \right] \cdot \frac{\partial}{\partial u} \left[\frac{\partial u}{\partial V'} \right] = \frac{\partial}{\partial u} \left[\frac{\partial \log G''}{\partial V'} \right] \cdot \frac{\partial}{\partial u} \left[\frac{\partial u}{\partial V''} \right],$$

so that the following ratio must be independent of β and of the V :

$$\frac{(\partial/\partial u)[\partial \log G'/\partial V]}{(\partial/\partial u)[\partial u/\partial V]} = \text{constant} = C^0.$$

This in turn requires the existence of a function $W^0(V)$ such that

$$\frac{\partial \log G'}{\partial V} = C^0 \frac{\partial u}{\partial V} + W^0(\bar{V}).$$

The term in C^0 can be eliminated by a trivial renormalization in which G' is multiplied by $\exp(-C^0 u)$ and the origin of β is translated by C^0 .

The term in $W^0(\bar{V})$ amounts to the multiplication by $\exp[\int W^0(\bar{V}) dV]$ of both the numerator and the denominator of the canonical distribution. Hence, this term vanishes.

To sum up, the second principle requires that—up to trivial renormalization—the function G' be independent of V , which means that it is adiabatically invariant. We know already that this condition is also sufficient to prove the second law, and that the integrating multiplier of dQ is in that case equal to β .

6. PERFECT GASES

In order to measure the β derived in the preceding sections, an instrument is needed. The usual procedure is to use a perfect gas thermometer, which is a physical system such that

$$\partial u/\partial V = u f(V).$$

7. GENERALIZATION OF THE SECOND LAW TO INDIVIDUAL CANONICAL SYSTEMS: THE RANDOM FORM OF THE CONCEPTS OF ENTROPY AND OF HEAT

Let us return to the situation at the end of Sec.3, where the canonical law has been established from either set of zeroth and first principles. The concept of "heat", as used in Secs. 4 and 5, was assumed to have been obtained by the usual method, which averages everything very early over a canonical distribution.

As a result, both Secs. 4 and 5 involve the *non-random* entropy

$$h = \beta E(U) + \log Z(\beta).$$

However, one frequently wishes to interpret "entropy" by the *random* expression:

$$h = \beta U + \log Z(\beta).$$

For example, h is necessary to give meaning to "Boltzmann's principle", that

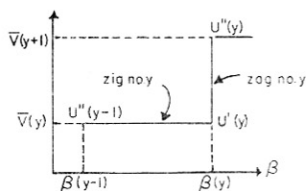
$$\text{"entropy"} = -\log(\text{probability of a state})."$$

This principle is in turn necessary to generalize the concept of entropy beyond its original context relative to equilibrium (that is, to the canonical law). Similarly, the methods based upon averaging raise difficulties concerning heat. In the verbal explanations of what is thermodynamics, one states that "heat" is a noncontrollable and presumably random portion of energy, while "work" is controllable and presumably nonrandom. However, by defining $\oint \beta E(dQ)$ with the sign E , that is by defining it for ensembles and not for systems, one immediately cancels out this distinction.

The above remarks describe the motivation of this section. We shall study the expression $\oint \beta dQ$ for an individual system, *without* averaging from the outset. "Heat" will remain a random quantity, but "work" will not; however, the averaging involved in the concept of "work" will be based on different grounds than is usual. The second law will be shown to apply to the *unaveraged* entropy and the Boltzmann's principle will be fully meaningful. Part of our discussion is closely related to that of Refs. 1 and 6.

⁶ L. Rosenfeld, *Physica* 27, 67 (1961).

Let us consider a physical system for which the path, that is, the sequence of its values of β and of the V_k , is an alternation of "zigs" during which β alone varies, and of "zags" during which β remains invariant, and let us parametrize the path by an index y , taking successive integral values at the points where one passes from one zig-zag to the next. The following graph summarizes various definitions.



Variation of temperature at fixed volume.

During a "zig", let our system be successively put in contact with a series of heat reservoirs, of slowly varying β , and let each contact be very long. The energy exchanged during each contact is of course a random variable and it will be interpreted as "heat". Clearly, the averaged "path-integral" $\oint \beta dE(Q) = \oint \beta dE(U)$ is trivially path-independent. But the unaveraged $\oint \beta dU$ might have depended upon intermediate random elements. Our main purpose here will be to show that such is not the case. For that, begin by dividing the "zig" into steps corresponding to equal increments of β . Then

$$\begin{aligned} \oint \beta dU &= \sum \beta(x)[U(x) - U(x - dx)] \\ &= U'(y)\beta(y) - U''(y-1)\beta(y-1) - dx \\ &\quad - \sum U(x)[\beta(x) - \beta(x-1)], \end{aligned}$$

the sum on the preceding line being carried over all the values of x except the first and last one. Let all the steps become infinitesimally small, while the contact with each successive heat reservoir remains sufficiently slow for the $U(x)$ to remain independent random variables. An easy application of a form of the strong law of large numbers shows that, with probability one,

$$\begin{aligned} \oint \beta dU &\Rightarrow U'(y)\beta(y) - U''(y-1)\beta(y-1) \\ &\quad - \oint E(U | \beta) d\beta, \end{aligned}$$

the averaging being due to a theorem and not to the fact that one has decided *a priori* to take account of ensemble averages exclusively.

Free and normal adiabatic changes of volume; the pressure.

Similarly, during the y th zag, the system acquires the random energy $U''(y) - U'(y) = U[\beta(y), \bar{V}(y+1)] - U[\beta(y), \bar{V}(y)]$. But this is not the whole story, since only part of this energy was contributed by heat reservoirs, the rest being contributed by the outside forces that changed \bar{V} . These two parts are respectively called "heat" and "work". Suppose that each zag is further subdivided into small steps, between which the system is put back into contact with a heat reservoir of temperature $1/\beta(y)$. Each minute change of volume requires an addition of energy which depends upon the initial and final volume and upon the initial energy, but not upon earlier values of energy; in particular, it is independent of the earlier temperature, and it can be designated by $(\partial u / \partial V_k) dV_k$. Such a change of volume is called "free adiabatic" and it does not in general preserve the canonical distribution: That is, let the same dV_k be applied to the members of a family of systems with a canonical energy; the energy of the perturbed systems needs not be canonical. Therefore, one replaces the "free adiabatic" changes by "normal adiabatic" changes, in which contact is recurrently reestablished with the heat reservoir of temperature $1/\beta$. Thanks to this canonical averaging, the exchange of energy due to changing V_k becomes independent of the intermediate energies of the system. By a further easy application of a variant of the strong law of large numbers, one finds that (with probability one) the exchanges of energy directly traceable to the changes dV_k are

$$\begin{aligned} \sum \oint \int dF(u | \beta, \bar{V}) (\partial u / \partial V_k) dV_k \\ = \sum p_k dV_k = dW. \end{aligned}$$

The p_k defined by this equality are called "generalized pressures", and dW defines the concept of "work", an asymptotically nonrandom part of the energy communicated to the system from the outside.

Consider now the rest of the energy exchanges, that is the exchanges during the successive intermittent contacts with the heat reservoir. This part is random and uncontrollable and it is natural to identify it as "heat"

Note that the above argument derives the concept of pressure and of work for individual canonical systems going through a series of small transformations. The usual verbal distinction

between the "disorderly" character of heat energy and the "orderly" character of work is formalized as the difference between random and nonrandom.

Now, putting the zigs and the zags together, one finds that

$$\oint \beta dQ = U'(F)\beta(F) - U''(0)\beta(0) - \oint \left\{ E(U | \beta, \bar{V}) d\beta + \beta \sum_k \left[\int dF(u | \beta, \bar{V}) (\partial u / \partial V_k) \right] \right\} dV_k.$$

Conclusion.

This leads us to the point where the usual discussion begins. The last integral is path-invariant if and only if its expected value is path-independent. If so,

$$dQ = H_{\text{final}} - H_{\text{initial}},$$

where H is the random entropy

$$H = \beta U + \log Z(\beta).$$

(This shows the invalidity of Khinchin's⁷ assertion, that H does not satisfy the "second law") Note that, when the path is closed, the entropy change does not necessarily vanish, because the initial and final values of U need not be equal.

Noncanonical systems, for which an entropy can be defined without using additional axioms.

Szilard¹ has shown that, when entropy is written as $\sum p_{\text{state}} \log p_{\text{state}}$, it can also apply to systems obtained from canonical systems by a free adiabatic transformation.

8. INCREASE PROPERTIES OF THE CANONICAL ENTROPY

We want to stress that the concept of entropy requires the second principle, which is unnecessary to derive the canonical law. This is why we insist upon avoiding any derivation of the canonical law that uses anything resembling entropy (or Shannon's "information"). More precisely, even if the use and the maximization of " $\log W$ " or " $-p \log p$ " is motivated on some axiomatic grounds, the maximum values of these expressions *cannot* be identified with entropy unless one introduces some additional statement equivalent to the second principle. But, if a second principle is used, one can derive the canonical law and the form of entropy. Let us

show that one can also derive some "increasing" properties of this entropy.

Irreversible changes of temperature.

Returning to the expression for $\oint \beta dU$; before the steps of β are made infinitely small $\oint \beta dU$ depends upon intermediate energy exchanges and can be greater or smaller than its limit for continuously varying β . But, considering expected values, one has

$$E \left[\sum \beta \Delta U - \int \beta dU \right] = \int E(U) d\beta - \sum E[U(x)] [\beta(x) - \beta(x-1)],$$

where $E[U(\beta)]$ is a decreasing function of β . Then, if β increases the above expression is the difference between the integral and a *lower* Riemann sum of a decreasing function. If β decreases, the above expression is the difference between an *upper* Riemann sum and an integral. Hence, for a closed loop, the expected value of $\sum \beta \Delta U - \int \beta dU$ is the difference between an upper and lower Riemann sum and it is *positive*.

Irreversible variation of volume.

The same argument holds, assuming that pressure is a decreasing function of every V_k .

9. GENERALIZATION OF THE SCOPE OF THERMODYNAMICS TO SYSTEMS WHICH ARE NOT IN EQUILIBRIUM AND CANONICAL

From the viewpoint of the core of results applicable to macroscopic systems, the results of the preceding sections are not a substantial improvement over the results of Sec. 5, relative to means. Moreover, for large systems, the fluctuations due to contact with a heat reservoir are so small in relative value, that the canonical theory gives acceptable predictions concerning most characteristics of isolated systems of fixed energy. However, to be able later to generalize thermodynamics beyond the results linked with the basic principles, it is necessary first to explicitly define a temperature and an entropy for isolated systems. For that, one must distinguish between work and heat. The path of the system, as sequence of values of (u, V_1, \dots, V_K) , will again be approximated by zig-zags. The "zigs" are free adiabatic and the energy change is the "work" $\sum (\partial u / \partial V_k) dV_k$. The "zags" correspond to an energy addition of $du - \sum (\partial u / \partial V_k) dV_k$, which is all heat. Temperature would be defined as a function of the V_k and of u , constituting an integrating divisor for heat; un-

⁷ A. I. Khinchin, *Mathematical Foundations of Statistical Mechanics* (Dover Publications, Inc., New York, 1949).

fortunately, the existence of such a multiplier requires a condition upon the expressions $(\partial u / \partial V_k)$, which was not necessary in the canonical case and has no reason of being generally satisfied. Hence, this method of generalizing the scope of thermodynamical concepts fails.

Of course, the definition of temperature for isolated systems is usually approached very differently. This temperature was discussed in reference 2. One knows that it loses all meaning when the energy u is known, but it is found convenient to give the same name to either one of a variety of functions of u , which converge for very large systems but differ for small ones. In reference 2 we have analyzed these functions and have noted that the choice of a definition of temperature bears the closest connexions with the basic problem of mathematical statistics: knowing that the quantity u is a sample value of a random quantity U , and that the distribution of U depends upon a parameter β , "estimate" the value of β from the value of u . It is intuitively true, and is confirmed by the theory, that estimation is a kind of guessing and is indeterminate except if one has a large number of sample values. But both the practice and the apparent intent of the operation "to define a temperature for an isolated thermodynamical system" can be interpreted as really meaning "to estimate the temperature of a heat reservoir, with which the isolated system should be presumed to have been in contact". For large systems, many estimates are equally good.

Let us now examine entropy. For isolated systems, the distinction between work and heat lacks here the clarity which it had in the canonical case. In order to define heat or work, one must define pressure and this is also done by an estimation procedure. By choosing appropriately a set of definitions of temperature and of pressure, one can arrange for the integral $\oint \beta dq$ to be path-invariant and thus define H . As a result, the number of useful definitions of entropy will be at least as large as the number of useful temperatures-in-isolation. The best known groups of definitions are the following:

Boltzmann's definitions. Temperature $1/\hat{\beta}_b$ is such that

$$u = E[U(\hat{\beta}_b)] = -\partial \log Z(\hat{\beta}_b) / \partial \hat{\beta}_b.$$

The pressures are $-(1/\hat{\beta}_b) \partial \log Z(\hat{\beta}_b) / \partial V_k$, and entropy is

$$\hat{h}_b = \hat{\beta}_b u + \log Z(\hat{\beta}_b) = \min_{\beta} \{\beta u + \log Z(\beta)\}.$$

Gibbs' differential definitions. Temperature is given by

$$\hat{\beta}_{gd} = (\partial / \partial u) \log [dG(u)].$$

The pressures are $(\partial / \partial V_k) \log [dG(u)]$, and entropy is

$$\hat{h}_{gd} = \log [dG(u)]$$

Gibbs' integral definitions. One replaces $dG(u)$ in the differential definitions by $G(u)$.

Note that nothing can be said in general concerning the sign of the difference between the Boltzmann and the Gibbs' entropies, the reason being that $\log [dG(u)]$ depends heavily upon the local regularity properties of $G(u)$, while the Boltzmann entropy does not.

Generalization of entropy. The usual generalizations of the concept of entropy are based upon a formal broadening of the conditions of applicability of either of the two relations:—Boltzmann's: "entropy = $\min \{-\log [\text{Pr (each "state" of energy } u)]\}$ "—Gibbs' differential: "entropy = $\log (\text{number of "states" of energy } u)$ ".

Either of these methods (and presumably other methods as well) will lead to a generalized theory. But the choice between them is largely arbitrary and hence controversial (they represent two methods of describing the role of the observer and of "information" in thermodynamics). One knows that, adding the right maximization criteria, either of the generalized definitions can replace the "zeroth principle" either in the classical sense or in our phenomenological sense. Hence, one may say that the generalization of thermodynamics hinges upon the zeroth principle.