of getting 6 events assuming negative α_{33} is 340 to 1 in favor of the destructive interference. This same type of calculation when made using the best-fit phase shifts to *all* the data will give artificially suppressed odds. This is because the experimental "low value" of the cross section at small angles will exert a strong effect in pulling the constructive interference curve part way down to it. In this case the ratio is only 11 to 1. We do not consider this experiment by itself as conclusive proof that α_{33} is positive, but when considered along with all the other evidence pointing toward an attractive $p_{\frac{3}{2}}$ interaction, the "odds" in favor of a positive α_{33} become overwhelming.

Some of the other evidence comes from the 65-Mev experiments at Columbia[2] and the 40-Mev experiments at Rochester[8] assuming charge independence. This is because the knowledge that α_{33} must become large as shown by the recent results from the Carnegie Institute of Technology[9] makes the Steinberger solution implausible. Also an attractive $p_{\frac{3}{2}}$ interaction is preferred theoretically in order to explain such large values of α_{33} as found in the 150 to 200-Mev region.[9] The values of the small angle scatterings below 30° are 17.9°, 19, 20, 23.4, 23.5, 23.6, 26.5, 27, 27.6, 28.9, 29.5, 29.6, and 29.7.

The earlier 110-Mev counter results of Anderson *et al.*[6] are fairly consistent with these plate results. Their values of a, b, and c at 110 Mev are 3.6 ± 0.7, -4.8 ± 0.8, and 7.5 ± 1.9 mb per steradian. Our values are 4.0 ± 0.4, -3.5 ± 0.7, and 6.8 ± 1.3. At 120 Mev their phase shifts are $\alpha_3=-15°$, $\alpha_{33}=30°$, and $\alpha_{31}=4°$. Ours are $-10.9°$, 27°, and $-3.2°$ at 113 Mev.

The data shown in Table I gave an M value of 11.8 when analyzed by the least squares method. M is the least squares sum in units of the standard deviations of each point. According to statistics the mean value of M should be 6 in the case of 9 experimental points and 3 parameters.[10] Since M is χ^2 distributed with $N=6$ in this case,[10] the probability that this experiment give $M\geqslant 11.8$ is 7 percent. Of course a small amount of d-wave might improve this fit, although the odds, 1 in 14, for having a fit as poor as this are not unreasonable. Inspection of Fig. 1 shows that the 9 experimental points alternate above and below the curve. We feel that this large M value is just a statistical oddity. To support this view a second least squares analysis was made. This time the data was divided into 6 equal units of solid angle giving $M=3.2$, which is very close to the expected mean value of 3 (for the case of 6 points and 3 parameters). Statistics would have to be improved in order to be sure of seeing any d-wave.

The author wishes to thank Mr. Paul Taylor, Mrs. Enid Bierman, and Mr. James Ross for their excellent job of scanning. Dr. Frank Solmitz kindly helped with the calculations and statistical problems which arose. In addition the author is grateful to Professor Enrico Fermi for helpful discussions.

[8] J. Tinlot and A. Roberts, Phys. Rev. **95**, 137 (1954).
[9] Blaser, Ashkin, Feiner, Gorman, and Stern, Phys. Rev. **95**, 624 (1954).
[10] H. Cramer, *Mathematical Methods of Statistics* (Princeton University Press, Princeton, 1946), Chap. 37.

PHYSICAL REVIEW VOLUME 96, NUMBER 5 DECEMBER 1, 1954

Method of Transition Probabilities in Quantum Mechanics and Quantum Statistics

P. T. LANDSBERG*
Randal Morgan Laboratory of Physics, University of Pennsylvania, Philadelphia, Pennsylvania
(Received February 23, 1954)

The concepts microscopic reversibility, detailed balancing, equal probabilities, equilibrium, H theorem are often used in (coarse grained) quantum statistics. It is pointed out that each has a (fine grained) quantum-mechanical counterpart. These concepts are formulated, and their interrelations discussed, at an abstract mathematical level. The results are then interpreted by taking first the fine grained and then the coarse grained point of view. A type of transition matrix arises which does not seem to have been investigated so far, and some of its properties are discussed.

1. INTRODUCTION

TWO starting points for quantum statistical mechanics and the statistical foundation of thermodynamics are often used. In the first one appeals at the outset to some principle of equal *a priori* probabilities and random *a priori* phases without making any attempt to establish these from more fundamental considerations. These assumptions make possible the introduction of ensembles into the theory. The microcanonical ensemble enables one to prove an H theorem for a perfectly isolated system in the following sense: if the ensemble is set up in accordance with an initial observation at a time $t=0$, when the value of H for the ensemble is $H(0)$, then, at all later times t, $H(t)\leq H(0)$. The statement "$dH/dt\leq 0$ at all times t" is definitely stronger, and, as far as we know, it has never been established from this kind of argument. By identifying H as a negative multiple of the entropy (S) one has here a restricted quantum statistical proof of the principle of the increase of entropy with time in a perfectly isolated system. The restriction resides in the fact that $S(t)\geq S(0)$ is weaker than $dS/dt\geq 0$. It

* On leave of absence from Department of Natural Philosophy, The University, Aberdeen, Scotland.

should, however, be noted that, by using a canonical ensemble for a system in essential isolation, the second law can be established in the unrestricted form (in Tolman's notation) $\Delta S \geq \int \delta Q/T$. This approach via ensembles is essentially the quantum-mechanical extension of Gibbs's statistical mechanics.[1]

The second approach, which is older, and is falling slowly into disuse, is associated with Boltzmann. Formulated in a modern manner, its object is to justify the use of ensembles. This is done by showing that the quantum-mechanical time average of macroscopically observable quantities in a closed system, and the microcanonical average of these quantities, taken at a fixed time, are almost always equal to each other. This is the quantum-mechanical ergodic theorem.[2] It holds if the number of macroscopically indistinguishable microscopic states is large enough, and if the energy levels of the system satisfy a certain restrictive condition.[3] The same conditions are sufficient (their necessity has not been proved) to establish the H theorem in the following sense: the time average of (a suitably defined) H for a quantum-mechanical system is approximately equal to the microcanonical average. While some of the concepts involved in this approach have been criticized,[4] it is more fundamental than the first approach, since it aims at being based on quantum mechanics, while the statistical assumptions play a subsidiary role. None the less, it is to be emphasized that this method also depends for its success upon an implicit assumption which is similar to that of equal *a priori* probabilities and random *a priori* phases.[5] This assumption occurs when one sets out to calculate the chances of finding conditions which are at variance with thermodynamics.

A third approach, which we shall call the method of transition probabilities, exhibits interesting differences. Its advantages are mathematical simplicity and a somewhat weaker statistical assumption. The method depends on an assumption of random *a priori* phases, but the principle of equal probabilities of accessible quantum states in equilibrium is not assumed, but is deduced by quantum mechanics.[6] The drawback of the method is that, it is valid only for limited time intervals, as will be discussed in Sec. 4. For these time intervals, it leads to the strong form $dH/dt \leq 0$ of the H theorem.

[1] R. C. Tolman, *Principles of Statistical Mechanics* (Oxford University Press, London, 1938).

[2] J. von Neumann, Z. Physik **57**, 30 (1929); W. Pauli and M. Fierz, Z. Physik **106**, 572 (1937); W. Pauli, Suppl. Nuovo cimento **6**, 166 (1949).

[3] If E_j be the exact energy levels of the system, we must have

$$E_j \neq E_k, \quad E_j - E_l + E_k - E_m \quad \text{for} \quad j \neq k, \quad l \neq m.$$

[4] E. C. Kemble, Phys. Rev. **56**, 1146 (1939).

[5] The author is indebted to Professor von Neumann for an opportunity to discuss this point with him.

[6] W. Pauli, *Probleme der modernen Physik*, edited by P. Debye (Hirzel, Leipzig, 1928), p. 30. See also T. Sakai, J. Phys. Soc. Japan **19**, 172 (1937); O. Halpern and F. W. Doerman, Phys. Rev. **55**, 1077 (1939); J. Davydov, J. Phys. (U.S.S.R.) **11**, 33 (1947).

We wish to emphasize that the older assumption of molecular chaos is replaced in all three approaches by an assumption concerning the perfect irregularity of certain phase constants.

The method of transition probabilities has recently been used in an interesting manner for the discussion of basic principles of statistical mechanics and thermodynamics.[7] The reason for taking up this problem again is that it seems desirable to develop the results a little further, and to clarify the foundations of this work with the following points in view. (1) It is essential in this type of discussion to make a clear distinction between coarse grained and fine grained probabilities. One must therefore introduce groups of microscopic states which cannot be distinguished by macroscopic methods. (2) It seems desirable to make explicit, and discuss separately, the assumption that, after a finite time, the probability that a system, chosen at random from the ensemble, is in its ith accessible state, becomes a constant. This would exclude fluctuations in ensemble averages,[8] and it is therefore best not to assume it automatically. (3) The assumption that all states of the systems in the ensemble are interconnected can be dropped altogether, and its effect investigated separately.

We shall set up our problem in abstract mathematical terms in Sec. 2, and offer the solution at the same level in Sec. 3. Thereafter we shall discuss the physical interpretation of the relations obtained, and show that the same mathematical scheme is useful from two entirely different points of view.

2. THE PRINCIPLES

Let W be a finite, positive, and nonzero integer. Let $G_1, \cdots, G_W$ be a set of finite, positive, and nonzero integers. Let $P_1, \cdots, P_W$ be a set of numbers which are continuous functions of the time t, such that $0 \leq P_j \leq 1$, $\sum_1^W P_i = 1$ at all values of t. Lastly, let A_{ij} $(i, j = 1, 2, \cdots, W)$ be a set of W^2 non-negative real numbers. All numbers, other than the P's are independent of t. The principles whose interrelations we wish to investigate are that for all $i, j = 1, 2, \cdots, W$:

$$A_{ij} = A_{ji}, \qquad (Q)$$

$$\textstyle\sum_j A_{ij} G_j = \sum_j A_{ji} G_i, \qquad (X)$$

$$P_i A_{ij} G_j = P_j A_{ji} G_i, \qquad (D)$$

$$A_{ij} \neq 0 \text{ only if } P_i/G_i = P_j/G_j, \qquad (P)$$

$$(P) \text{ holds for a nonzero interval of } t. \qquad (P')$$

$$\dot{P}_i \equiv \frac{dP_i}{dt} \equiv \sum_i (P_j A_{ji} G_i - P_i A_{ij} G_j) = 0, \qquad (Eq)$$

$$\dot{H} \equiv \frac{dH}{dt} \equiv \frac{d}{dt}\{\textstyle\sum_i P_i \log(P_i/G_i)\} = 0, \qquad (H')$$

$$\dot{H} \leq 0. \qquad (H)$$

[7] J. S. Thomsen, Phys. Rev. **91**, 1263 (1953).

[8] In finite ensembles fluctuations may have to be considered.

Unless stated otherwise, each principle is assumed to hold only at a certain value of t, so that our inferences will be of the form if (A) is valid at t, then (B) is valid at t. However, in the case of the first two principles it is clear that if they hold at a certain value of t, then they hold at all values of t. We shall write $(A)\rightarrow(B)$ for (A) implies (B), but (B) does not imply (A); and $(A)\rightleftharpoons(B)$ for (A) implies (B), and (B) implies (A). $(A)+(B)\rightleftharpoons(C)+(D)$ shall mean that if one assumes both (A) and (B), one can deduce both (C) and (D), and conversely. It is assumed that $A_{ii}=0$ for all i.

The question as to the extent to which any one of these principles, or some combination of these principles, implies others, presents clearly a problem in pure mathematics, and is fully defined by the above information. Its solution is attempted in the next section.

3. THE THEOREMS

Lemma 1.—If the quantities P_i are arbitrary (except for the condition $\sum P_i=1$), then in order that $\dot{H}$ be an extremum with respect to P_r, when all other P's are kept fixed, P_r must satisfy

$$\mu=F_r-\sum_{j=1}^{W}\left\{\frac{G_r}{P_r}A_{jr}(P_jG_r-P_rG_j)+A_{rj}G_j\log\frac{P_jG_r}{P_rG_j}\right\},$$

where μ is a constant which does not depend on r, and

$$F_r\equiv\sum_{i=1}^{W}(A_{rj}-A_{jr})G_j.$$

The proof depends on the use of a Lagrangian multiplier μ to ensure that the P's are normalized.

Lemma 2.—If the conditions of Lemma 1 are fulfilled for every $r=1, 2, \cdots, W$, and if $F_r=0$ for every r, then condition (P) holds. $\dot{P}_1, \dot{P}_2\cdots, \dot{P}_W$, and $\dot{H}$ all vanish as a consequence.

Proof.—Consider a pair of suffixes with the properties $A_{st}\neq0$, $P_s/G_s>P_t/G_t$, and another pair with the properties $A_{uv}\neq0$, $P_u/G_u<P_v/G_v$. We must consider four possibilities. (α) A pair of suffixes of both types exists. (β) A pair of suffixes like (s, t) exists, but no pair exists with the properties of the pair (u, v). (γ) A pair of suffixes with the properties of the pair (u, v) exists, but no pair exists with the properties of the pair (s, t). (δ) No pair of suffixes exists which has either property. Situation (α) can be ruled out as follows. Of all suffixes $s, t; u, v$ consider one of those for which P_j/G_j has its largest value, and let this suffix be $j=a$. Consider also one of those suffixes $s, t; u, v$ for which P_j/G_j has its smallest value, and let this suffix be $j=b$. On choosing $r=a$ in Lemma 1, one finds $\mu>0$. On choosing $r=b$ in Lemma 1, one finds $\mu<0$, and this is a contradiction. Situations (β) and (γ) can be eliminated without reference to Lemma 1.[9] Since

$$\dot{P}_i=\sum_jG_iG_j\left(\frac{P_j}{G_j}-\frac{P_i}{G_i}\right)A_{ji}-P_iF_i,$$

and $F_i=0$, $A_{ji}\geq0$, it follows that $\dot{P}_i\geq0$ for all i. Now $\dot{P}_t>0$, so that $\sum_i\dot{P}_i>0$. This contradicts the normalization conditions, and situation (β) must therefore be ruled out. A similar argument eliminates (γ), since one would find $\sum_i\dot{P}_i<0$. This leaves only situation (δ) which implies that if $A_{ij}\neq0$, then $P_i/G_i=P_j/G_j$. Hence $\dot{P}_i=0$ for all i. Therefore,

$$\dot{H}=\sum_i\dot{P}_i\log(P_i/G_i)=0.$$

Interpretation of Condition (P). Our W suffixes can be subdivided into groups according to the following rule. For any pair of suffixes x, y within the same group it must be possible to form a nonzero product of A's of the form:

$$\text{either } A_{xa}A_{ab}\cdots A_{fg}A_{gy} \text{ or } A_{ya}A_{ab}\cdots A_{fg}A_{gx}.$$

Let the smallest number of groups of suffixes obtainable in this manner be v, and let the αth group contain w_α suffixes. It follows that

$$\sum_1^v w_\alpha=W,\quad A_{ij}=0 \text{ if } i, j \text{ belong to different groups.}$$

If i and j be in the same group, A_{ij} *can* be zero, but it *need not* be zero. Again in some cases one may have some w_α's which are unity; in others no subdivision of suffixes into groups may be possible, so that $v=1$. This subdivision of the suffixes into groups is independent of the value of t, since it depends only on the properties of the A's.

If now (P) holds at a certain value of t, we find simply that for all i within a group of suffixes the value of P_i/G_i is independent of i, and depends only on α. Suppose that for all i within the αth group $P_i/G_i=K_\alpha$ $(\alpha=1, 2, \cdots, v)$. One can then arrange the v groups of suffixes according to the size of K_α, e.g., so that

$$K_1\leq K_2\leq\cdots\leq K_v,$$

and this will be assumed whenever (P) holds. If (P) holds and $v=1$, then $K_1=1/W$ in virtue of the normalization condition.

As a simple application of these ideas, we note from the result,

$$\dot{H}=\sum_{i,j}(P_jA_{ji}G_i-P_iA_{ij}G_j)\log(P_i/G_i),$$

that each group of suffixes contributes to $\dot{H}$ a value which is independent of the other groups. Thus the total value of $\dot{H}$ is simply a sum of the contributions to $\dot{H}$ which arise from each group of suffixes. Our next lemma deals with a typical contribution to $\dot{H}$ when condition (P) holds very nearly.

Lemma 3.—If for all i in the αth group of suffixes $P_i=K_\alpha G_i(1+\Delta_i)$, $|\Delta_i|\ll1$, where K_α is a non-negative constant, then the contribution to $\dot{H}$ from the αth group of suffixes is given by

$$2\dot{H}=-K_\alpha\sum_{i,j}G_jA_{ji}G_i(\Delta_j-\Delta_i)^2-K_\alpha\sum_iG_iF_i\Delta_i(1+\Delta_i).$$

[9] Alternatively, the argument used for case (α) may also be applied in these cases.

The proof depends only on some algebraic manipulations.

Theorem 1.—$(Q)+(D) \to (P)+(D) \to (D) \to (Eq) \to (H') \to H$.

$(Q)+(D)$ implies $P_iA_{ij}G_j=P_jA_{ij}G_i$. If $A_{ij}\neq 0$, $P_iG_j=P_jG_i$ follows. Thus $(Q)+(D)$ implies (P), so that $(Q)+(D)$ implies $(P)+(D)$. On the other hand if

(i) $$A_{ij}=0,\quad A_{ji}\neq 0,\quad P_i=P_j=0,$$

then (P) and (D) are both satisfied, but (Q) is violated. This shows that $(P)+(D)$ does not imply (Q). Again, $(P)+(D)$ obviously implies (D), but (D) does not imply (P), as shown by the following example:

(ii) $$W=2;\ G_1=G_2=1;\ P_1=\tfrac{1}{3},\ P_2=\tfrac{2}{3};\ A_{ij}=\begin{pmatrix}0 & 2\\ 1 & 0\end{pmatrix}.$$

This satisfies (D), but violates (P). Again (D) implies (Eq), as follows immediately from the definition of $\dot{P}_i$. That (Eq) does not imply (D) is proved by the following example:

(iii) $$W=3;\quad G_1=G_2=G_3=1;$$
$$P_1=\tfrac{1}{6},\quad P_2=\tfrac{1}{3},\quad P_3=\tfrac{1}{2};\quad A_{ij}=\begin{bmatrix}0 & 6 & 12\\ 6 & 0 & 3\\ 2 & 4 & 0\end{bmatrix}.$$

This leads to (Eq) and to

$$P_1A_{12}=P_2A_{23}=P_3A_{31}=1,\quad P_2A_{21}=P_3A_{32}=P_1A_{13}=2,$$

so that it contradicts (D). Since

$$\dot{H}=\textstyle\sum_i\dot{P}_i\log(P_i/G_i),$$

(Eq) implies (H'). The converse does not hold, as shown by example (IV).

(iv) $$W=3;\quad G_1=G_2=G_3=1;$$
$$P_1=P_2=P_3=\tfrac{1}{3};\quad A_{ij}=\begin{bmatrix}0 & 1 & 1\\ 1 & 0 & 0\\ 2 & 0 & 0\end{bmatrix}.$$

By the definition of $\dot{P}_i$ this leads to

$$\dot{P}_1=\tfrac{1}{3},\quad \dot{P}_2=0,\quad \dot{P}_3=-\tfrac{1}{3},$$

thus satisfying (H'), but violating (Eq). The result $(H') \to (H)$ is obvious.

Theorem 1a.—If $v=1$, then $(P)+(D)$ implies (Q).

If there is only one group of suffixes and (P) holds, then $P_i=G_i/W>0$ for all i, so that $(P)+(D)$ implies $G_iA_{ij}G_j/W=G_jA_{ji}G_i/W$ (all i,j), and this leads to (Q).

Theorem 2.—$(Q)+(D) \to (Q) \to (X) \to (H)$.

Obviously $(Q)+(D)$ implies (Q). The converse is untrue, as proved by Example (v).

(v) $$W=2;\ G_1=G_2=1;\ P_1=\tfrac{1}{3},\ P_2=\tfrac{2}{3};\ A_{ij}=\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}.$$

This satisfies (Q), but contradicts (D). The result $(Q) \to (X)$ is obvious from the definitions. Now (X) implies $F_i=0$ for all i, and imposes no restriction on the P's, so that Lemmas 1 and 2 apply. Hence $\dot{H}$ attains its extreme value with respect to each P_r if (P) holds, so that, as a consequence, $\dot{H}=0$. On the other hand, if (X) holds but $\dot{H}$ does not attain its extreme value, then $\dot{H}<0$ by Lemma 3. Hence (X) implies $\dot{H}\leq 0$, and this is (H). The converse is disproved by Example (iv). This implies $\dot{H}=0$, so that (H) holds, but it contradicts (X).

Theorem 3.—$(Q)+(D)\rightleftharpoons(Q)+(Eq)\rightleftharpoons(Q)+(P)$.

Since $(Q) \to (X)$ (Theorem 2), and (X) implies $F_r=0$ for all r, one can use Lemmas 1 to 3. Since $(D) \to (Eq)$ (Theorem 1), therefore $(Q)+(D)$ implies $(Q)+(Eq)$. Since $(Eq) \to (H')$ (Theorem 1), the maximum value of $\dot{H}$, whose existence is implied by (Q), is actually attained, so that (P) holds by Lemma 2. Thus $(Q)+(Eq)$ implies $(Q)+(P)$. Lastly, it is clear that (Q) implies (D) if A_{ij} or A_{ji} are known to vanish. If neither vanishes, however, $(Q)+(P)$ implies $A_{ij}(P_i/G_i)=A_{ji}(P_j/G_j)$, and this is again (D). Thus $(Q)+(P)$ implies $(Q)+(D)$, and this establishes the complete equivalence of the above three propositions (from each one the other two can be deduced).

Theorem 4.—$(P)+(D) \to (P)+(Eq)\rightleftharpoons(X)+(Eq)\rightleftharpoons(X)+(H')\rightleftharpoons(P') \to (X)$.

Since $(D) \to (Eq)$ (Theorem 1), therefore $(P)+(D)$ imply $(P)+(Eq)$. The converse is disproved by the following example:

(vi) $$W=3;\quad G_1=G_2=G_3=1;$$
$$P_1=P_2=P_3=\tfrac{1}{3};\quad A_{ij}=\begin{bmatrix}0 & 1 & 2\\ 2 & 0 & 0\\ 1 & 1 & 0\end{bmatrix}.$$

This satisfies (P) and (Eq), but contradicts (D). Again, $(P)+(Eq)$ implies that

$$\dot{P}_i=\sum_j G_iG_j\left(\frac{P_j}{G_j}A_{ji}-\frac{P_i}{G_i}A_{ij}\right)=\sum_j G_iG_j\frac{P_i}{G_i}(A_{ji}-A_{ij})=0.$$

Hence $\sum_jG_j(A_{ji}-A_{ij})=0$ (all i), and this is (X). Since, in addition, $(Eq) \to (H')$ (Theorem 1), it follows that $(X)+(Eq)$ implies $(X)+(H')$. Again, if $(X)+(H')$ hold a certain value T of t, then, by Lemmas 2 and 3, at $t=T$, (P) holds, and $\dot{P}_i=0$ for all i. Since we have just shown that $(P)+(Eq)$ implies (X), it follows that (X) must hold at $t=T$, and therefore (X) holds at all values of t. If the first change of a P_i away from its value given by condition (P) occurs at $t=T'$, then we must have $d^nP_i/dt^n=P_i[\sum_jG_j(A_{ji}-A_{ij})]^n\neq 0$ for some positive integer n, and for some i at $t=T'$, and this would imply that (X) fails for some i. This is a contradiction, so that $(X)+(H')$ implies (P'). Again, (P') implies clearly (P) as well as (Eq), since for the nonzero interval of t for which (P) is valid, all P_i are given by equations of the form $P_i=K_\alpha G_i$ (i in group α of suffixes), and are therefore independent of t. This proves the equivalence of the four intermediate propositions of Theorem 4. Lastly, $(X)+(H')$ clearly implies (X). That (X) does not imply either (P) or (Eq) is proved by Example (v).

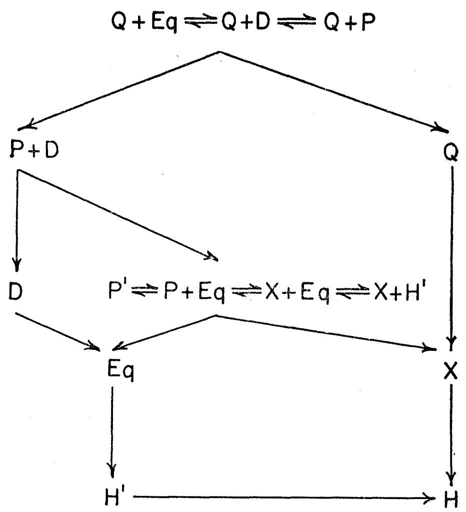

FIG. 1. General scheme of implications. $A \rightarrow B$ means that if (A) is true of the ensemble of duplicates of a certain system at time T, then (B) is also true of this ensemble at that time. The converse, (A) follows from (B), does not hold. $A \rightleftharpoons B$ means that both the direct result and its converse apply.

Theorem 5.—$(X)+(Eq) \rightarrow (Eq)$.

It must merely be shown that (Eq) does not imply (X). This is accomplished by Example (iii).

A summary of the relations established is given in Fig. 1. Inspection of the figure raises the question if a relation of implication can be established between a pair of the following three proposition: (Q), (D), $(X)+(Eq)$, or between the following two propositions: (X), (Eq). However, this can be shown to be impossible. Example (v) shows that (Q) does not imply (D) or (Eq). (D) does not imply (Q) or (X) [Example (ii)]. $(X)+(Eq)$ does not imply (Q) or (D) [Example (vi)]. Again, (X) does not imply (Eq) (Theorem 4), nor does (Eq) imply (X) (Theorem 5).

4. THE TWO POSSIBLE INTERPRETATIONS

(A) By way of physical interpretation of the above formalism, we consider an ensemble of identical systems whose energies lie all in the same small energy range $(E, E+\Delta E)$. W is interpreted as the number of different macroscopically distinguishable states $i=1, 2, \cdots, W$ which each system of the ensemble can exhibit. However, each state i may be any one of a group of G_i microscopically distinct states, between which our measurements cannot distinguish. P_i is interpreted as the probability of finding a member of the ensemble in the state i, i.e., in the group of G_i macroscopically indistinguishable states. Alternatively we may say that P_i is the probability, as averaged over a microcanonical ensemble, of finding the system of interest in the state i. P_i is a so-called "coarse grained" probability; the P_i's go over into "fine grained" probabilities as W is increased and the integers G_i decreased until $G_1=G_2=\cdots=G_W=1$. If the P's are coarse grained probabilities, H is then the quantity, characteristic of an ensemble, which occurs in the quantum-mechanical H theorem. From it one can obtain the statistical mechanical analog of the second law of thermodynamics, by noting that the quantity $S=-kH$ has the required properties of the entropy. (Eq) states that, as far as can be ascertained by the macroscopic measurements under consideration, the ensemble averages of the various physical quantities exhibited by the system of interest have constant values. In general, such a situation can arise only if the fluctuations in the ensemble averages can be neglected (e.g., if the macroscopic measurements are sufficiently coarse, and extended over a sufficiently short period). Thus (Eq) postulates ensemble equilibrium (as revealed by the measurements under consideration). The principle (P) is most easily interpreted if it is assumed that the system can reach each of the W macroscopic states from every state i. If this assumption of the interconnection of states is adjoined to (P), then (P) states $P_i=G_i/W$ for all i. This is simply the principle of equal *a priori* probabilities (at equilibrium) of all accessible microscopic states.[10] The statement (P) is just the required generalization of this principle when one does not wish to make an assumption as to the interconnection of states. The A's are transition probabilities per unit time, and (Q) is a statement of a result, concerning transitions and inverse transitions, which depends on the Hermitian character of the perturbation operators, and on an assumption concerning random phases. (Q) is sometimes referred to as the principle of microscopic reversibility. (D), on the other hand, equates the transition rate $i \rightarrow j$ and the transition rate $j \rightarrow i$, so that it may be regarded as a statement of the principle of detailed balancing for transitions between macroscopically distinguishable states.

The time independence of the A's is the basic assumption which underlies our discussion. It applies in fact only to systems whose Hamiltonian can be split into an unperturbed part, for which the Schrödinger equation can be solved, and a sufficiently weak perturbation. Hence, if at least one of the states between which transition is made belongs to a practically continuous spectrum of unperturbed energy levels, one arrives at A's which are independent of the time for certain restricted time intervals.

(B) The mathematical discussion of Sec. 3 admits of an alternative interpretation, which is free of all statistical elements. In this approach the P's are the fine grained probabilities and the G's are all unity. The basic limitation of the discussion resides again in the assumed existence of time-independent transition probabilities A_{ij}, but the assumption of random phases is not now involved, and (Q) is an exact quantum-me-

[10] Our principle (P) is a generalization of the principle (E) of reference 7, which is there called the ergodic hypothesis. We reserve this name here for a hypothesis which relates time averages of probabilities to ensemble averages of probabilities. Jordan calls the principle (E) Liouville's theorem for quantum statistics. We prefer to adopt as the latter one of Tolman's formulations.

chanical result (provided, of course, the perturbation operator and the time satisfy the usual requirements). But there is not now any contact, through the condition (*H*), with the macroscopic measurements of thermodynamics, even though a theorem corresponding to the *H* theorem can again be proved, and is not in this case based on an assumption of random *a priori* phases. All the results which one obtains by adopting this fine grained point of view are to be regarded as results in quantum mechanics proper, and not as results in quantum statistical mechanics.

Strictly speaking all principles of Sec. 2, excepting (*Q*) and (*X*), are thus seen to be principles which may or may not apply to an ensemble of duplicates of a system of interest. Their truth or falsehood is therefore characteristic of the ensemble rather than of the system itself.

5. DISCUSSION

We first of all adopt interpretation (B), which uses the fine grained probabilities. In this case (*Q*) may be taken as correct, and hence leads to (*H*). The proof, freed from the assumption as to the existence of transition probabilities, is due to Klein.[11] But this is a result in quantum mechanics, and therefore not the *H* theorem proper. To investigate the limiting value which *H* approaches, we adjoin to (*Q*) the assumption (*Eq*), and deduce from Fig. 1 the validity of both (*P*) and (*D*). Thus, if the states i and j are connected (directly or via other states), the P_i and P_j tend to become equal. This is the well-known effect of quantum-mechanical "spreading," which has no classical analog. Assuming the interconnection of states, Jordan[12] has already observed that $(Q)+(Eq)$ implies equal probabilities for different states.

In interpretation (A) the proof that the assumption of random phases leads to (*Q*), and that (*Q*) in turn implies (*H*) is due to Pauli.[6]

We wish to emphasize the very limited part which the interconnection of states can play in these considerations. Theorem 1a represents the only example we have found of a relation of implication which holds only if this assumption is made, and Fig. 2 represents the scheme of implications for this case. On the other

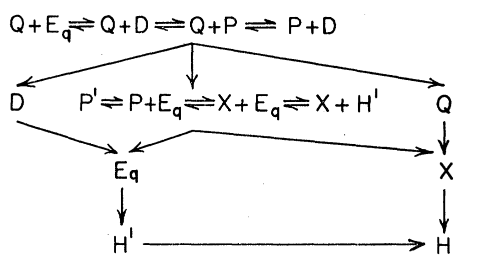

FIG. 2. Scheme of implications, provided the states $i, j, \cdots$ are interconnected. See caption of Fig. 1.

[11] O. Klein, Z. Physik **72**, 767 (1931).

[12] P. Jordan, *Statistische Mechanik auf Quantentheoretischer Grundlage* (Vieweg, Braunschweig, 1933), p. 25.

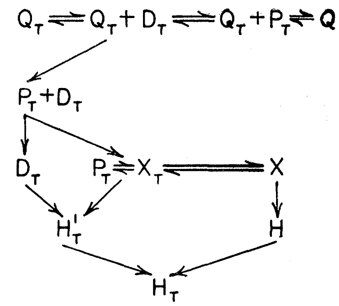

FIG. 3. Scheme of implications, provided the ensemble attains the condition (*Eq*) at some time (*T*). See caption of Fig. 1.

hand, the assumption of equilibrium in the stringent form (*Eq*) is very powerful. Figure 1 shows that if at a certain time (*Q*) be true and (*Eq*) be false (e.g., due to fluctuations in ensemble averages about a mean value), then (*X*) and (*H*) must also be true, but (*P*), (*P'*), (*D*), and (*H'*) must all be false at that time. Yet, restrictive though the equilibrium assumption (*Eq*) is, it alone does not enable one to infer the existence of detailed balancing.

It may possibly be of interest to draw attention to the time-independent condition (*X*) which does not appear to have been noticed before (it is a generalization of Thomsen's λ hypothesis).[7] It is sufficient to deduce the *H* theorem, and, if (*H'*) be adjoined to it, it implies (*P*), even (*P'*), as well as (*Eq*). The implication in some writings that the validity of (*Q*) is a necessary condition for the validity of the *H* theorem, is therefore not correct.

As an example of a series of stipulations in which each is more restrictive than the preceding one, we may note the following: If (*P*) holds at a time *T* for a certain system *S* (more accurately: for the ensemble of duplicates of a certain system *S*), this does not imply that any of the other statements of Sec. 2 shall be true of *S* at *T* or at any other time. If (*P*) and (*Eq*) are both true of *S* at time *T*, however, (*H'*) must hold at time *T*, while (*X*), and therefore (*H*), must be true of *S* at time *T*, and therefore also at all other times. Neither (*D*) nor (*Q*) need be true of *S* at any time in this case. If (*P*) and (*D*) are both true of *S* at time *T*, this is a more restrictive condition, in that (*D*) must now definitely be true of *S* at time *T*. (*Q*) need still not be true of *S* at any time. Lastly, if (*P*) and (*D*) be both true of *S* at time *T*, and the states are interconnected, then all the other principles of Sec. 2 must be true of *S* at time *T*. In particular, (*Q*), (*X*), and (*H*) are then true of *S* at all times.

As a further example of the use of Figs. 1 and 2, let us consider now a system such that the ensemble of its duplicates attains the condition (*Eq*) at some time *T*. Let us denote by (A_T) a principle if it is true of the ensemble at the time *T*, and let (*A*) denote the same principle if it is true of the ensemble at all times. The schemes of Figs. 1 and 2, give them rise to those of Figs. 3 and 4, which are self-explanatory.

Figure 4 incorporates all assumptions made by Thomsen,[7] provided our *G*'s are set equal to unity. It

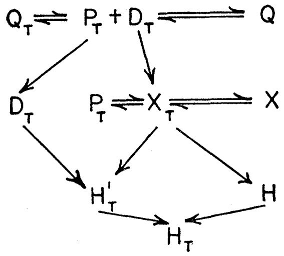

FIG. 4. Scheme of implications, provided the assumptions of both Figs. 2 and 3 are made. See caption of Fig. 1.

should therefore be compared with his results which are summarized in Fig. 5. The only significant difference is seen to reside in the fact that his principle (S) and our principle (H) do not occupy analogous positions, although they are both supposed to represent the statistical counterpart of the second law of thermodynamics. The reason resides in Thomsen's Theorem 3, in which he proves that (S) implies (P_T). In the present treatment it is impossible to prove such a theorem, as evidenced by our example (iii). This shows that (H) may be valid, even for an indefinite period of time, without enabling one to infer (P), (X), or (D): and that this remains true even if the condition (Eq) is adjoined to (H). The H theorem is therefore seen to imply only comparatively weak restrictions on the parameters of the theory. This is also clear on the general grounds that (H') and (H) each represent just one restrictive equation which is to be imposed on the parameters at any one time, whereas all the other conditions represent several restrictive equations.

6. SIGNIFICANCE OF THE CONDITION (X): COARSE GRAINED TRANSITION MATRICES

In this section, we wish to consider briefly the properties of those transition matrices A which satisfy the condition (X). Such considerations belong properly to the theory of matrices whose elements are real and non-negative. This was initiated by Frobenius,[13] and has been developed more recently by other authors.[14,15] Such matrices are also of importance in the theory of probability,[16,17] and, in particular, in connection with Markov processes.[18] In these theories one often studies stochastic matrices, i.e., matrices whose elements are real and non-negative, and whose row sums are unity. Occasionally doubly stochastic matrices are also studied. In such matrices the elements in any one row and in any one column add up to unity. If we agree to take any one row sum in an order defined by the requirement that the column suffix shall increase, and any one column sum in the order indicated by an increasing row suffix, and if we also agree to give the jth term in any one such sum the finite and nonzero weight G_j, we shall speak of the "weighted" row sum and of the "weighted" column sum. A matrix which satisfies condition (X) is clearly not a stochastic, or a doubly stochastic, matrix; it is a matrix whose jth weighted row sum is equal to its jth weighted column sum for all $j=1, 2, \cdots W$. A matrix satisfying this requirement for some set of weights G_j, and having all its elements non-negative, will be said to be a "coarse grained" transition matrix. We shall establish some of its properties.

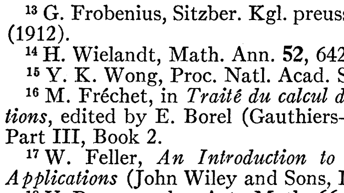

FIG. 5. Scheme of implications deduced by Thomsen (see reference 7). The symbols Q, D_T, P_T, X correspond to Thomsen's symbols M, D, E, L, respectively.

Let $B(p,q)$ be a matrix of p rows and q columns. Let O denote a matrix whose elements are all zero. Frobenius[13] defined a matrix B as *decomposable* if it could be expressed in terms of submatrices according to the scheme

$$B(n,n)=\begin{pmatrix} P(a,a) & Q(a, n-a) \\ O(n-a, a) & R(n-a, n-a) \end{pmatrix}, \quad 1\leq a\leq n-1, \quad (1)$$

by applying a permutation to the row suffixes, and the same permutation to the column suffixes. If Q is also a zero matrix, B is said to be *completely decomposable.*

Theorem 6.—If a coarse-grained transition matrix is decomposable, then it is completely decomposable.

Proof.—Let $A(n,n)$ be the matrix under consideration, and let the weighting factors be $G_1, \cdots G_W$. Let G be a diagonal matrix whose (j,j) element is G_j, and let a matrix B be defined by $B\equiv GAG$. The sum of the jth row of B is then equal to the sum of the jth column of B [by condition (X)]. B can be decomposed as in (1), since A is decomposable; also the elements of the matrices P, Q, R are all non-negative. Now the sum of the first a rows of B must be equal to the sum of the first a columns of B. But the difference between these two sums is the sum of the elements of Q, and this must therefore be zero. Hence B is completely decomposable. It follows that A is completely decomposable.

Theorem 7.—If a matrix $A(n,n)$ whose elements are non-negative is not decomposable, then the quantities $(A^r)_{jk}$ $(r=1, 2, \cdots, n-1)$ cannot all vanish for any given pair of suffixes j,k.

This result is due to Frobenius.[19] The quantities $(A^r)_{jk}$ are just the products which we introduced in Sec. 2.

[13] G. Frobenius, Sitzber. Kgl. preuss. Akad. Wiss. Berlin, p. 456 (1912).
[14] H. Wielandt, Math. Ann. **52**, 642 (1950).
[15] Y. K. Wong, Proc. Natl. Acad. Sci. **40**, 121 (1954).
[16] M. Fréchet, in *Traité du calcul des probabilités et ses applications*, edited by E. Borel (Gauthiers-Villars, Paris, 1938), Vol. I, Part III, Book 2.
[17] W. Feller, *An Introduction to Probability Theory and its Applications* (John Wiley and Sons, Inc., New York, 1950).
[18] V. Romanovsky, Acta Math. **66**, 137 (1935).
[19] See reference 13, p. 461.

Theorem 8.—By applying the same permutation to the rows and columns of a coarse grained transition matrix the latter may be completely decomposed into indecomposable parts, or it is itself indecomposable.

This result follows from the last two theorems. As a special case, we note that "fine grained" transition matrices, for which $G_1=G_2=\cdots G_W=1$, and doubly stochastic matrices, are all completely decomposable.

By Theorem 8 condition (X) ensures that the W macroscopically distinguishable states can be subdivided into groups of states such that no transitions are possible between groups, while transitions *in either direction* are always possible between any two states which belong to the same group. Thus, whatever the values of the weighting factors G_j, condition (X) ensures that if transitions are possible from a state j to a state k (possibly via other states), then converse transitions are also possible.

The author is indebted to Dr. J. S. Thomsen for a careful reading of the manuscript, and a resulting helpful discussion.

APPENDIX

In this appendix we shall derive two additional results, which, while not essential to the main arguments of the text, will serve to clarify the relations obtained.

In Lemma 3 we have neglected terms of order Δ_j^3, and this will now be justified by showing that the terms in Δ_j^2 must in all important cases make some contribution.

Lemma 4.—If condition (P) can hold for a system, then, when it holds very nearly and at least one Δ_j of Lemma 3 is nonzero, we must have

$$\sum_{i,j} G_j A_{ji} G_i (\Delta_j-\Delta_i)^2>0 \quad (i,j \text{ in } \alpha\text{th group of suffixes; valid for all } \alpha).$$

Proof.—When condition (P) holds, the probability of finding one of the suffixes i is

$$\sum_{i=1}^{w_\alpha} P_i=K_\alpha \sum_{i=1}^{w_\alpha} G_i.$$

This equation must remain valid even when (P) does not hold, as no transitions are possible between different groups of states. Hence

$$\sum_{j=1}^{w_\alpha} \Delta_j=0.$$

Thus, if one Δ_j, Δ_k say, is nonzero, we must have $w_\alpha>1$ and, also, there must exist at least one other nonzero Δ_j, Δ_l say, which has a sign opposite to that of Δ_k. The states k and l can be joined by a nonzero product of the A's, and, by definition, this can be formed using only suffixes from the αth group. Let it be $A_{ka}A_{ab}\cdots A_{pq}A_{ql}$. We can now show that, if Lemma 4 were not true, one could arrive at a contradiction.

Suppose, then, $\Delta_k\neq 0$, $\sum_{i,j} G_j A_{ji} G_i (\Delta_j-\Delta_i)^2=0$. Then each term in this sum must vanish separately. Consider those terms of this sum which are specified by the pairs of suffixes: $(i,j)=(k,a)$, (a,b), $\cdots$ (p,q), (q,l). Since the A's are nonzero for these terms, they will vanish separately only if $\Delta_k=\Delta_a=\Delta_b\cdots\Delta_p=\Delta_q=\Delta_l$. Since Δ_k, Δ_l are of opposite sign and nonzero, this is a contradiction. Hence Lemma 4 holds.

It follows from this lemma that in the neighborhood of $\dot{H}=0$, for which $\dot{H}\neq 0$, $\dot{H}$ is in fact negative, provided $F_r=0$ for all r. Under these conditions $\dot{H}$ must attain a maximum value when $\dot{H}=0$. This result is used in Theorem 3.

Theorem 1b.—If $(P)+(D)$ holds (so that $P_i/G_i=K_\alpha$ for all v groups $\alpha=1, 2, \cdots, v$ of suffixes), and if $K_\alpha>0$ for all α, then (Q) holds.

Consider the αth group of suffixes. Suppose $P_i/G_i \neq P_j/G_j$, then $A_{ij}=A_{ji}$ by (P), so that (Q) holds in this case for the αth group of suffixes, there being no need to appeal to (D). Suppose next $P_iG_j=P_jG_i$. By (D) $P_iA_{ij}G_j=P_jA_{ji}G_i$, and these two results enable one to deduce (Q) for the αth group of suffixes also in this case, provided $P_i>0$. But, by hypothesis, $K_\alpha=P_i/G_i>0$, so that (Q) is established for the αth group of suffixes in both cases. Repeating the argument for the other groups of suffixes, the proposition is finally proved.

If the states are interconnected, $v=1$ and $K_1=1/W>0$, so that the conditions of Theorem 1b are fulfilled. Hence,

Theorem 1a.—If the states are interconnected, then $(P)+(D)$ implies (Q).

It is therefore clear that Theorem 1b is somewhat stronger than Theorem 1a of the main text.